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**VARNISH
MAKING**

**The
MODERN
CHEMICAL INDUSTRIES
SERIES**

VARNISH MAKING

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The MODERN CHEMICAL INDUSTRIES SERIES.

General Preface.

The present work belongs to a series of handbooks published under the general title of The Modern Chemical Industries Series. The aim of these books is to give a clear, straightforward description—written from a technical standpoint—of present-day manufacturing operations and their scientific control.

The scope embraces modern plant and practice only. Special attention is given to the methods and equipment used in evaluating materials and controlling processes. The authors, in each case, are men of recognised technical ability, with actual works experience.

Special precautions are taken to avoid the inclusion of obsolete processes and matter of purely scientific or historical interest. On the other hand, equal care has been taken to avoid anything approaching the "catalogue" style. The books are intended to embody the experience of industrial chemists gained in everyday practice.

Each volume is devoted to a single industry, or group of related industries, and the final volumes will include a General Index to the whole series. They will also include such additional matter as is required to ensure the series being a self-contained library covering the entire range of the chemical and allied industries. This arrangement confers a flexibility which enables additions and revisions to be made when and where required ; it ensures—and this is vitally important to technical literature—a continuous growth in the most economical manner possible.

H. B. C.

VARNISH MAKING

PREFACE

THE present volume is written primarily for the student who desires to obtain a practical knowledge of the manufacture of various types of varnishes together with sufficient theoretical knowledge to understand the principles on which the processes are based and the standards by which his products will be judged.

During recent years there have been great advances as regards both the theory and the practice of varnish manufacture. Much of the theoretical work involves a considerable knowledge of advanced physical chemistry and although, so far as possible, the more academic aspects of the subject have been avoided it is hoped that sufficient has been said to stimulate the reader's interest and to impress upon him the necessity of continuing his studies and consulting some of the more scientific works to which reference is made in the text.

On the practical side there have been developments in respect of raw materials, particularly synthetic resins, and the use of China wood oil, while new methods of heating and heat transfer have been developed. There has also been a marked increase in the attention paid to the problem of recovering the volatile matter lost in the process of gum-running. In its traditional form the process of gum-running involves the loss of nearly 25 per cent by weight of a comparatively expensive material. There is no need to emphasise that this is a serious matter, quite apart from the fact that it also involves considerable trouble and expense to the varnish maker in the disposal of the waste material and avoidance of committing a nuisance.

The production of a good varnish is a matter requiring much skill and experience. The best and most suitable materials can easily be spoiled. Practical examples are given

of the various types of varnishes and it is suggested that the student should commence experiments by making up varnishes on the basis of 100 grammes of resin. The successful transference of this laboratory experiment to the works, however, invariably requires considerable modifications owing to the changed conditions involved in the use of much larger quantities of material. With the experience gained in making a small laboratory batch, however, it is possible to advance in a larger batch using, say, three or four pounds of gum and from this proceeding to a full-scale works charge.

As regards the laboratory testing of varnishes, details have been given of the simpler chemical tests and particular attention has been paid to the practical and physical tests which are of the most immediate importance. It is hoped in this way to give the student not only a thorough grounding in the subject but also to guide him in his reading and practical studies as he proceeds to more advanced work.

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VARNISH MAKING

CHAPTER I

INTRODUCTORY

VARNISHES are generally divided into two classes : oil varnishes and spirit varnishes. Oil varnishes consist essentially of resin compounded with a vegetable oil, the combination being thinned down to working consistency by the addition of volatile thinners. When spread out into a film, such a varnish dries first by the evaporation of the solvents, and finally by the oxidation and possibly polymerisation of the residual non-volatile matter. The spirit varnishes, on the other hand, consist merely of a solution of resin in a volatile solvent, and in this case, therefore, drying is essentially a process of evaporation, though the properties of the residual film are determined by complicated relationships between the solvent and the resin, the study of which involves many aspects of the properties of colloidal substances.

It is usual to include under the term "varnishes" a third class of material, in which the resins are replaced either wholly or partially by bituminous substances. In some cases these bodies are combined with oil before the addition of the thinners, while in others they are dissolved directly in a solvent. Bituminous varnishes may, therefore, be included with both the oil varnishes and the spirit varnishes, but, owing to the fact that they are in many respects distinct products, as regards their properties and their application in industry, they are dealt with separately in the present work.

The properties of the individual raw materials are dealt with in the subsequent chapters, but a general review of their properties and functions may be conveniently made at the present stage.

1a. *Natural Resins.* The resins used in varnish manufacture

are vegetable products exuded from various trees as the result either of intentional or accidental wounding. The properties vary according to the age of the resin and its botanical origin. Generally speaking, the older the resin the harder it becomes. Thus the hardest resins are the fossil resins of East Africa, which have lain in the soil (probably) for many centuries since they exuded from trees which have long since disappeared. On the other hand, the resins from certain trees, notably that producing Sierra Leone copal, become extremely hard even within a short period after exudation. Generally speaking, however, recently exuded resins are comparatively soft.

From the point of view of varnish manufacture, the chief criteria of quality are the solubility either in oil or in volatile solvents and the hardness and elasticity of the film. The resins used in oil varnish manufacture are, in their natural condition, insoluble in oil even on prolonged heating, but if they are heated considerably above their melting point for some time they are partially decomposed, and when this decomposition has proceeded to a certain point the residue is soluble in hot linseed oil.

The term "solution" is here used in a very wide sense. Strictly speaking, the mixture forms a more or less stable colloidal system, and the art of the varnish manufacturer consists largely in conducting his operations in such a way that the system will remain permanent and unchanged almost indefinitely, provided it is effectively protected from oxidation and evaporation. If a varnish is badly made it is quite possible that although it may appear to be quite satisfactory for a short time, or even for as much as a month or two after manufacture, it will change more or less rapidly, finally producing a quite useless material.

The other type of resin, namely, that used in spirit varnishes, is soluble in certain volatile substances. In this case the suitability of the resin is determined by the completeness and stability of the solution.

These spirit soluble resins may be divided into two main classes: resins soluble in alcohol (methylated spirits), and damars, which are soluble in coal-tar hydrocarbons (benzene and naphthas), turpentine, and also in petroleum distillates (white spirit). Generally speaking, the solution in white spirit is not so stable as that in coal-tar hydrocarbons.

1b. *Synthetic Resins.* The use of resinous substances produced by chemical means has become very general during recent years. These synthetic resins are extremely complex, and in most cases their intimate chemical structure is still a matter for discussion. The number of chemical reactions which produce such substances is very large, and new products are still being offered to the varnish maker at a bewildering rate.

Some of these resins should strictly speaking be described as modified natural resins, as they consist essentially of natural resins of a high acid content combined with other substances; for example, the "Albertols" are phenol formaldehyde condensation products combined with natural resins such as rosin or manila copal, yielding oil-soluble resins. Similar products are also obtained by combining phthalic anhydride-glycerol (glyptal) condensation products with natural resins.

Resins of these two types are the most commonly used in the varnish industry. The method of using them has been the subject of much research by the makers, and very full directions are published in their pamphlets.

These substances are discussed in Chapter VIII., but the subject of synthetic resins is so complex and the resins are so numerous that the reader who is interested must be referred to standard works on the subject.

At the present time the literature dealing with synthetic resins is being added to daily and the whole subject is in a state of rapid development. The student must therefore keep himself well informed of current events.

At the same time, it must be emphasised that the basis of success in the use of synthetic resins is the same as that in the use of natural resins—careful attention to detail and a due appreciation of the nature of the relation between oil and resin in varnish and the physical and chemical changes brought about by heat treatment.

A thorough grasp of the principles of varnish manufacture with natural resins is the only safe basis for successful handling of the synthetic product.

2. *Oils.* The oil most commonly used in varnish manufacture is, of course, linseed oil, but during recent years China wood oil has been largely used. Whichever oil is employed, it is necessary that it should be free from impurities and

carefully refined before the oil can be safely used in varnish manufacture.

In the case of linseed oil, refining is necessary to remove not merely extraneous matter—dirt and particles of seed—but also certain substances, mainly albuminoids, which coagulate on heating. Although a raw oil may appear quite clear and sparkling, it will, on heating to about 250° C., deposit a more or less thick cloud of coagulated material, commonly known in the trade as “spawn.” As the process of varnish manufacture involves heating, it is obvious that these substances must be removed before the oil can be used in varnish manufacture.

3. *Volatile Thinners.* Volatile thinners used in varnish manufacture have increased greatly in number during the last generation. Formerly, turpentine was the only one considered legitimate, but in 1885 Samuel Banner patented a special grade of petroleum distillate which he called “white spirit,” and which corresponded fairly closely in volatility with turpentine. Since that time the use of white spirit has increased enormously, partly on account of its particular technical qualities and partly because it is very much cheaper than turpentine.

The solvent properties of white spirit are very different from those of turpentine and in the early days much trouble arose through lack of appreciation of these differences. It has also to be borne in mind that petroleum distillates from different oils are of different composition and have correspondingly differing solvent properties. White spirit, however, has become an essential raw material from the varnish manufacturer's point of view and by the skilful adaptation of methods he is able to produce excellent varnishes with it.

These two materials, turpentine and white spirit, are the principal thinners and solvents used by the varnish maker. In addition, the coal-tar hydrocarbons are used to a considerable extent while certain special preparations frequently included in the varnish maker's list of products involve the use of such substances as the chlorinated hydrocarbons, organic esters, and other synthetic materials. The range of these is ever being increased, but the use of them is very largely confined to the cellulose lacquer industry.

4. *Bitumens and Pitches.* Bitumens and pitches are largely

used in the manufacture of stoving varnishes, black enamels and lacquers. The natural bitumens are obtained from various parts of the world and show almost as wide a variation in properties as do the natural resins.

In addition, an important series of pitches is obtained from the residues of the distillation of crude mineral oils and of crude coal tar. These are all used to varying extents in the varnish industry.

5. *Driers.* In the case of oil varnishes, the residue left on the evaporation of the volatile solvents is in the form of a sticky film, the conversion of which to a hard protective coating depends very largely upon oxidation. This is a comparatively slow process requiring many days but it can be accelerated by the incorporation of certain metals which act as catalysts so that the varnish becomes dry in the course of about twenty-four hours; in fact some modern varnishes will dry in as little as four hours. These metals, the chief of which are lead, cobalt and manganese, are incorporated with the oil either by a process of heating suitable compounds with the oil, in which case they combine directly with the oil, or they can be added subsequently to the finished oil resin mixture in the form of salts such as the resinates and linoleates which are soluble in the thinners.

As in the case of resins, it requires considerable judgment and skill to effect the combination of the drier with the other ingredients of the varnish in such a way that the system remains stable and the driers are not subsequently precipitated from the varnish, thus not only spoiling it from the point of view of clarity but changing its drying properties.

From the above short summary it will be seen that the varnish maker has to deal with a wide range of very varied materials. The selection of any one of them for the production of a varnish is an extremely important matter, involving great judgment and experience. It is, therefore, necessary for the student to make himself familiar with as wide a range of these materials as possible and carefully to compare their properties.

It is often possible to effect considerable economies both in time and money in the manufacture of varnish by a judicious selection of the raw materials. The quality of the product obtained depends to so large an extent upon the skill and knowledge of the maker that it is by no means uncommon for

a skilled varnish maker to turn out a far better product with what might be termed inferior materials, than a less skilled man could produce, given the highest grade materials regardless of cost.

There is also the further point to be considered, namely, that, particularly in the case of resins, even with the greatest care both on the part of the gum merchant and the purchaser there is bound to be a considerable variation in the properties and quality of the deliveries and consequently the varnish maker must always be prepared to modify his process to some extent, and however familiar he may be with the manufacture of a particular varnish must always be quick to observe any peculiarities in the behaviour of a new delivery of raw material.

The existence of so great a variety of raw materials naturally affords great scope for ingenuity and skill in buying. Prices are continually fluctuating and therefore the choice of the right moment at which to buy a given quality and the deciding of the quantity to be purchased are matters on which correct judgment may often make all the difference between financial success and failure. It may, of course, be said that this is not the function of the varnish maker, but although the actual purchasing may be done by the buying department, it rests very largely with the varnish maker to say what shall be purchased and how much. It is, therefore, necessary for him to take an intelligent interest in market prices and to make himself well acquainted with the rate at which each raw material is consumed and the stocks which it is possible to carry. He is thus able to supply the buyer with accurate information and may often save many thousands of pounds in the course of a year by intelligent foresight and organisation of his factory methods.

In the following pages these various points will be dealt with in more detail and the reader is strongly advised to extend his studies to include at least some of the more elaborate works and important papers to which reference is made in the text.

CHAPTER II

FACTORY SITE AND LAY-OUT

GENERALLY speaking, the varnish technologist has to be content with the factory as he finds it. It is well, however, to consider the particular requirements of the industry with reference to the position of the factory and its design. As regards the first, there is always the possibility of starting a new factory and, even in the case of an old one, the knowledge of what is ideal is very often of the utmost value in designing and adapting an existing site so as to compensate for its geographical shortcomings, while in respect of the lay-out the possibility of extension must always be borne in mind by any progressive firm.

Apart from the internal economy of his factory, the varnish maker is strictly limited by two considerations : (1) the fact that his industry is, even under the most efficient conditions, liable to create objectionable odours in the neighbourhood and therefore he must either choose a site well away from residential quarters or take elaborate precautions to avoid committing a nuisance ; and (2) owing to the fact that he uses highly inflammable materials and at the same time requires a considerable amount of more or less open heating, he is particularly liable to danger from fire.

As regards the site of the factory, it is evident that he must give careful consideration to this question of the amenities of the neighbourhood ; in fact if he does not do so the local authorities will soon remind him of his obligations and he will be involved in endless troubles which in the long run will prove more expensive than would be the case had a more suitable site been chosen at first or more efficient means of avoiding noxious odours installed when building the new factory.

TRANSPORT

These conditions being satisfied, the varnish maker will

require a considerable area of reasonably flat land, preferably near a canal and a railway. The advantage of water transport is particularly obvious in the case of the varnish industry which involves the use of large quantities of raw material that can be stored for a considerable time. Consequently, provided intelligent foresight is exercised in buying, speedy delivery is not of importance for the bulk of the materials such as linseed oil and resins. Water transport in bulk is far cheaper than any other form of transport and therefore is to be desired.

The desirability of proximity to a railway is equally obvious from the point of view of despatching finished materials to customers. The rapid development of road transport has also to be considered, especially as many of the varnish makers' products are of an inflammable character and therefore suffer under restrictions in the matter of railway transport. An efficient road transport service is therefore a great advantage.

FUEL AND LIGHT

Both gas and electricity play an important part in modern industry and in choosing a site it is important that the varnish maker should make himself well acquainted with the local rates and also the cost involved in bringing the mains into the works.

WATER SUPPLY

An adequate water supply is also desirable, for although water does not enter into the actual processes of varnish making, the use of condenser plant in connection with fume-recovery and other water-cooled plant is increasing and, of course, steam is required in most places for power purposes, although electricity is increasingly employed.

FIRE RISKS

As regards the design of the factory, it is advisable that it should be fairly well scattered so that the portions which involve the risk of fire, such as oil-boiling and gum-running, can be carried out well away from the other operations of the factory. Small fires are almost inevitable in these operations, but if the workmen are well trained and the factory properly designed they can be easily put out and, in fact,

soon come to be regarded without any undue excitement. Fires, of course, are to be avoided so far as possible but at the same time it is necessary to arrange things so that the men concerned in them can put them out quickly and without "losing their heads."

Fires are most likely to occur in the process of gum-running, sometimes due to the presence of impurities in the resins, which cause it to froth more vigorously than usually, or due to overheating.

In the case of oil-boiling, when large quantities are being heated, it sometimes happens that the temperature gets out of hand and even if the fire is drawn the oil continues to increase in temperature, due to oxidation, at such a rate that it may spontaneously ignite. An excessive draught of air across the top of a varnish pot may sometimes cause it to ignite. However, if the pots are quickly covered these fires are not dangerous provided no other inflammable material is in the immediate neighbourhood. Obviously, the operation of adding the thinners to the oil must be conducted well away from the oil-boiling and gum-running shed.

BUILDINGS

As regards the various factory buildings, a liberal supply of storage space is essential. Oils are stored in large tanks and provision must be made for several hundred gallons even in a comparatively small factory. Quite apart from the desirability of being able to carry large stocks and thus enabling the buying department to replenish them at the most suitable time from the point of view of market prices, vegetable oils improve considerably on keeping, and even if rapid methods of refining are adopted, tankage of several weeks is essential in order to ensure the settling-out of all suspended impurities.

This applies still more to the finished varnish. Some of the best varnishes even to-day are stored for as long as two years, and though the adoption of modern methods of filtering and clarification shortens this period it is undoubtedly necessary that varnishes should be "aged" for at least two or three months. Adequate tankage for the finished varnishes is therefore essential.

The more inflammable substances such as turpentine and white spirit which are purchased in bulk, may need a separate

storing place situated well away from the gum-running and oil-boiling plant. In the case of petrol and liquids with a flash-point below 73° F., government regulations are enforced as to design and position of the storage of any considerable quantity, and these should be strictly observed by the varnish maker, in his own interests.

Resins are invariably stored in bins and it is important that the "gum house" should be a dry and well-ventilated building and that the receptacles for the resin should be well protected from both moisture and dirt. Many resins oxidise slowly and some soften at comparatively low temperatures. It is therefore desirable that they should be kept as cool as possible and precautions taken to keep the room clean and orderly.

CHAPTER III

LINSEED OIL

LINSEED oil is obtained from the seeds of the flax plant (*Linum usitatissimum*), which is grown in vast quantities for the production of both flax and oil. Unfortunately, however, the varieties which produce the best flax do not produce the greatest proportion of the oil. The variety grown for the seed is branching and short in the stem, seldom exceeding 20 in. high, whereas that which produces the best flax fibre has a straight, unbranched stem which grows to about 3 ft. in height.

The cultivation of the plant, therefore, varies according to the product which it is most desired to obtain. In Canada, for example, in the prairie provinces, linseed is grown for the seed only, while in Ontario it is grown for both seed and flax.

When it is desired to produce a high quality flax fibre, the plants are sown closely together to encourage the production of a long, unbranched stem. On the other hand, where seed is required the plants are sown widely apart in order to allow free branching.

At the present time the most important linseed-producing countries are the Argentine, India, United States of America, and Canada, the Argentine crop of over two million tons being by far the largest.

As regards the English supplies, about two-thirds of the seed comes from the Argentine and practically the whole of the remainder from India. In 1932, England imported over 24,000 tons of linseed oil and 364,000 tons of linseed, of which 345,000 tons came from the Argentine.

The oil is extracted from the seed by one of two methods, crushing or solvent extraction. In the first method the seed is cooked and then placed in cages and subjected to pressure usually by means of hydraulic rams. The oil is thus forced out and run into storage tanks where the impurities are

allowed to settle out. The cakes left in the press are used as cattle food, and in this country linseed oil cake forms an important item of the oil-crusher's business; in fact, he is invariably termed an oil cake manufacturer. As the nutritive value of the cake depends to a considerable extent upon the amount of oil left in it, the 5 to 10 per cent which is not expelled by the crusher is not to be considered as wasted.

On the other hand, on the Continent the demand for cattle food in the form of cake is not so great, and consequently, the tendency is to adopt a method which removes practically the whole of the oil, this being under the circumstances the more useful product. The solvent-extraction process is, therefore, preferred. In this process the linseed is first ground to a meal and then placed in large containers and flooded with gasoline. After allowing sufficient time for the oil to be dissolved the solution is run off and the volatile solvent removed by distillation and used again.

REFINING LINSEED OIL

Whichever process is used, linseed oil requires refining before it can be used by the varnish maker. As already stated, the raw oil contains albuminous substances which cannot be removed by filtration but are precipitated by heating the oil. Various chemical methods of refining the oil have been suggested. The two principal ones are acid-refining and alkali-refining. In the first process sulphuric acid is used and the oil finally obtained is comparatively high in acid value. In the second process the free fatty acids of the oil are, of course, neutralised and the oil produced is practically free from acidity.

The latter process is, therefore, used where oil is required for edible purposes but the former is still largely employed in the production of oils for paint and varnish manufacture.

Of recent years there has been increased interest in methods of refining which avoid the use of active chemicals and which depend more upon the fact that the albuminous impurities are coagulated by heat. The oil is heated to a sufficiently high temperature to coagulate the albuminous substances and then a bleaching agent such as fuller's earth is added. The oil is then filtered by one of the methods referred to in the chapter on varnish filtration. The oil thus prepared is

suitable for paint and varnish manufacture and has a very good colour and low acidity.

TANKED OIL

In the paint trade the term "raw oil" is used to cover all linseed oils which have not received any special refining treatment and it therefore includes oil which has been tanked. During storage the bulk of the "foots" is precipitated and oil which has been tanked for some months gives no precipitate on heating. At the same time, the constant changes of temperature and contact with the air to a limited extent, produce certain changes in the oil and in process of time the complex mixture of glycerides attains its most stable form. The oil therefore undergoes a kind of natural refinement. Tanked oil is largely used, particularly by painters when it is necessary to reduce the consistency of their paints and although usually called "raw oil" is quite distinct from the product which comes direct from the oil mill, and, as already described, is an impure product.

HEAT REFINED OIL

This process is based on the fact already mentioned that the raw mucilage contained in untanked oil is precipitated on heating. One is thus able to eliminate a large part of the tanking period.

From 500 to 1,000 gallons of oil are usually treated at one time. The oil is heated to about 360° F. at which temperature it usually "breaks," i.e., the mucilage is precipitated. It should be noted, however, that the temperature at which precipitation occurs depends on the rate of heating and the nature of the oil. In the laboratory when using only a small quantity of oil the temperature may reach 520° F. before it breaks. It is therefore necessary that the heating process should be very carefully observed. When precipitation has occurred the oil is filtered. It is necessary that this should be done while the oil is hot as the mucilage may partially re-dissolve as the oil cools (see R. S. Morrell, Bibliography). In order to facilitate filtration it is necessary to add a filter aid such as kieselguhr or fuller's earth in order to prevent the slimy material from clogging the filters. Even when a centrifugal machine is used the addition of a filter aid is

advantageous. Oils prepared in this way are used very largely in the manufacture of varnishes and paint media.

ALKALI REFINED OIL

Oils refined by this process are practically free from acid and very pale in colour. The process is therefore used in preparing oils for edible and pharmaceutical purposes. From the varnish maker's point of view there is no particular advantage in using oils so refined ; indeed, the entire absence of free acids increases the tendency to precipitation in many types of varnish, and owing to the large amount of foots found in varnishes made with alkali-refined oil the cost of manufacture is higher.

ACID REFINING

In the acid refining process about one per cent of concentrated sulphuric acid is added to a large batch of the oil contained in a steam-heated vat provided with an efficient stirring gear, the temperature being kept at about 120° F. The acid will attack the linseed oil as well as the albuminous matter and, therefore, it is necessary that the process should be carried out with great care and the temperature kept as low as possible, certainly not exceeding 160° F. If this is done properly the impurities are first attacked and the oil left comparatively pale. If, of course, the acid attacks the oil itself to any considerable extent the oil becomes darker in colour and is therefore not suitable for the manufacture of pale, high grade varnishes.

When the refining action has proceeded far enough water is added, the stirring gear stopped, and the whole allowed to settle. The lower layer which contains the sulphuric acid and the bulk of the impurities is run off. The remaining oil is then usually transferred to another vessel where it can be washed very thoroughly with water or, preferably, with a very dilute alkaline solution until completely free from mineral acids. If this is done properly the resulting oil is much paler than the original raw oil and the acid value should not exceed 12 (milligrammes of potash per gramme of oil).

Formerly, it was the custom for the varnish maker to refine his own oil and usually he used the sulphuric acid method just described, but with the increasing tendency

towards mass production and specialisation it is becoming more and more usual to leave the refining of oil to be carried out by other concerns.

Whatever method of refining is used, it is desirable that the oil should be tanked for a considerable time so that all impurities settle out. Apart from this, however, other changes appear to occur which possibly involve a high degree of oxidation and generally improve the quality of the oil.

THE PROPERTIES OF LINSEED OIL

The value of linseed oil in the varnish industry depends fundamentally upon two properties :

1. When exposed to the air it reacts with the oxygen of the atmosphere forming ultimately a tough insoluble substance called "linoxyn."

2. On heating it gradually thickens so that finally an almost solid substance can be obtained. This thickening is due to the property of polymerisation, that is, the molecules of the compounds present in the oil combine among themselves, forming larger groups.

The first property, that of forming an oxidation product, is, of course, the one on which the drying of both paints and varnishes mainly depends. The second property, however, is extremely important as it enables one to obtain a series of oils of viscosities ranging from that of the raw oil to an almost solid, stringy mass.

OXIDATION OF LINSEED OIL

Linseed oil, in common with all other vegetable oils, consists of a mixture of glycerides of various fatty acids. Its distinctive property is that it contains a very high proportion of the more unsaturated acids ; it is therefore able to take up a correspondingly larger proportion of oxygen, and, moreover, does so at an increased rate.

The composition of linseed oil varies to some extent according to the conditions under which the plant is grown, but is generally of the following order :

Saturated fatty acids	...	...	...	10 per cent
Oleic acid	...	...	...	5 " "
Linolic acid	...	...	...	48 to 59 per cent
Linolenic acid	...	...	...	21 " 32 " "
Glyceryl radical	...	...	...	4.6 per cent

Four series of fatty acids, differing in their degree of unsaturation, are represented in the above table :

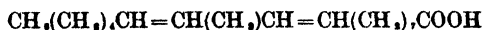
1. *Stearic Acid Group.* The acids of this group are saturated ; that is to say, they are incapable of combining by direct addition with other elements such as oxygen, hydrogen, iodine, or chlorine. They have the general formula $C_nH_{2n}O_2$, stearic acid itself being $CH_3(CH_2)_{16}COOH$.

2. *The Oleic Acid Group.* The acids of this group contain one double bond and are therefore capable of combining with two atoms of hydrogen or halogen. The general formula of the series is $C_nH_{2n-2}O_2$. The ordinary oleic acid obtained from vegetable oils has the formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$.

Various other acids can also be prepared, each differing from oleic acid only in the position of the double bond. It is usual to indicate the position of the double bond by numbering the carbon atoms, starting with the one in the carboxyl group (COOH). Thus the ordinary acid is described as 9—10 acid.

The position of the double bond has a very important bearing upon the power of the acid to combine with other elements by addition. Thus the ordinary oleic acid (9—10), when treated with iodine in the usual method of determining the iodine value of an oil, will absorb 80 per cent of its weight of iodine, whereas the oleic acid which has the double bond between the second and third carbon atoms will absorb only 3—18 per cent of iodine under the same test.

3. *The Linolic Acid Group.* The general formula of the acids of this series is $C_nH_{2n-4}O_2$. They contain two double bonds and are thus capable of absorbing four atoms of hydrogen or halogen. The formula for linolic acid is probably :

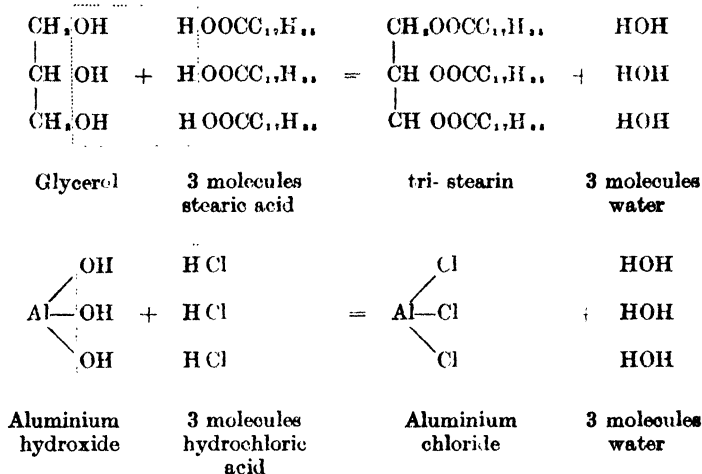


4. *The Linolenic Acid Group.* The acids of this series have the general formula $C_nH_{2n-6}O_2$. They contain 3 double bonds and are therefore capable of combining with 6 atoms of hydrogen or halogen. The formula of linolenic acid is believed to be :



These acids are present in both vegetable and animal oils combined with glycerol, which is an alcohol containing 3

hydroxyl groups and therefore capable of combining with the acids in the same way as the inorganic tri-basic substances, such as aluminium hydroxide, will combine with a monobasic acid such as hydrochloric acid.



It will be seen that each molecule of glycerol can combine with 1, 2 or 3 molecules of a monobasic fatty acid or even with 3 single molecules of 3 different fatty acids. The number of possible combinations between the fatty acids present in linseed oil with the glycerol is, therefore, very great and it is not in our present state of knowledge possible to state with certainty exactly what glycerides are present in a given oil.

THE DRYING OF OILS.

The actual process of drying is not quite so simple as would appear from these formulæ, various complications being introduced mainly by reason of the presence of the glycerol with which the fatty acids are combined in the oil. As a matter of fact, the fatty acids themselves do not dry in such a way as to produce a suitable paint oil, so that it is evident that the mere addition of oxygen at the double bonds in the acid portions of the molecule cannot possibly afford a complete explanation of the phenomena of drying.

It is not proposed at this stage to go into the subject of the mechanism of the oxidation or drying of linseed oil but the

reader may be referred to the chapter on drying oils in R. S. Morrell's book, "Varnishes and their Components."

Whatever may be the final explanation of the phenomena of drying, it may be said that for practical purposes the value of the linseed oil is determined so far as drying is concerned by the amount of unsaturated fatty acids in combination with the glycerol which are present in the oil, and therefore the iodine value (see page 119) is, from the point of view of the paint and varnish maker, a very important check upon the quality of the oil.

It has already been mentioned in the introduction that the drying process can be greatly accelerated by the use of catalysts and a very important operation in the varnish factory is the production of *boiled oils*, i.e., oils in which sufficient amounts of metallic catalysts have been added to produce a rapid-drying oil.

When a linseed oil is exposed to the air in the form of a thin film it is found that the weight of the film increases very slowly at first. Then follows a period of very rapid increase in weight, followed by a period in which the rate of increase in weight decreases, until finally there is a slight decrease in weight. The total increase in weight is of the order of 17 per cent, but during this time there is also a loss of material in the form of carbon dioxide, water vapour and small amounts of various organic compounds formed by the decomposition of the glyceride. The actual weight of oxygen absorbed is of the order of .25 per cent.

Both the rate and extent of drying are greatly influenced by the actinic power of the light and the presence of moisture in the atmosphere. Under normal conditions the oil attains its maximum increase in weight after about eight or nine days. With the proper amount of catalysts added this may be reduced to as many hours.

It has been found by experiment that using single metals the best results are obtained with the following proportions :

Lead	...	...	...	...	...	0.50 per cent
Manganese	...	...	...	...	...	0.05 " "
Cobalt	...	...	...	...	...	0.03 " "

Even better results are obtained with a mixture of metals. Typical combinations are lead and manganese, the proportions being 0.7 per cent lead and 0.02 per cent manganese.

Other authorities, however, are of the opinion that this is rather too high a proportion of lead and that 0.5 per cent lead and 0.05 per cent manganese is better.

Cobalt metal is usually used alone but sometimes added in small proportions with lead or manganese. Generally speaking, it works better with manganese than with lead.

Although the general effect of these metals is to decrease the drying time, there are important differences in their behaviour. Thus it is usually found that the drying of an oil containing a lead drier is less affected by moisture and by the normal changes of temperature than that of one containing either manganese or cobalt. Cobalt drier, on the other hand, is a very rapid drier and gives a harder film than does lead.

BOILED OIL

The term "boiled oil" is used in the trade to cover all linseed oils to which driers have been added even though the process of manufacture does not involve heating. The following are typical methods of procedure :

1. The oil is heated to about 520° F. and the driers added in the form of oxides or salts—usually acetates, resinates or borates—and heating continued until combination with the oil is complete.

The compounds most commonly used are :

Lead oxide usually litharge (PbO), lead acetate, preferably in the anhydrous form, and lead borate. The acetate and borate are to be preferred as they yield a paler oil.

Manganese oxide usually the dioxide (MnO_2) which, however, gives a dark oil especially when the mineral form, pyrolusite, is used. The sulphate, borate and oxalate are used in the preparation of pale oil the borate being the most generally used. It should be noted that the composition of commercial manganese borates is not very definite and consequently it is necessary to determine the metallic content of the variety to be used.

Cobalt is usually used in the form of resinate or linoleate, but sometimes the acetate is boiled into the oil as in the case of manganese and lead.

The oils obtained by this process are usually dark in colour

depending on the temperature and duration of heating which, of course, also affect the viscosity.

2. The metals to be used as driers are added in the form of resinates or linoleates which dissolve readily at temperatures below 160° C. Oils obtained in this way are paler than those prepared by the first method. This method is particularly adapted for use when the varnish pot can be heated either electrically or by oil as described on page 28.

3. A concentrated drying oil is made by dissolving the linoleates or resinates in a portion of the oil, and this is added to the bulk of the oil in such amount as to give the desired metallic content in the finished oil. In this way it is possible to avoid actually heating the bulk of the oil and a very pale product results.

THICKENED OILS

When linseed oil is heated it gradually thickens and increases in specific gravity. This change is due to polymerisation, that is, combination between the molecules of glyceride composing the oil. The rate at which the change occurs depends upon the temperature, and in practice the oil is heated to about 550°—570° F. A series of "stand" oils can thus be obtained, the thickest commercial grades being very stringy and semi-solid.

In the paint industry, however, only the comparatively thin grades are used, the thicker oils being largely employed in the manufacture of printing ink, and are, therefore, generally called lithographic varnishes or "litho oils," although their use is not confined to making lithographic inks. The following is the result of an examination of a series of these thickened oils :

SPECIFIC GRAVITY.			VISCOSITY.
15.5° C.			POISES AT 15.5° C.
Linseed oil	...	.935	0.6
"Ex. tint"	...	.958	19.5
"Tint"	...	.966	71.7
"Thin"	...	.967	86.9
"Mid"	...	.973	350.8

In the paint trade, the stand oil in general use is usually rather thinner than the "ex. tint" varnish in the above table. It is customary for the purchaser to specify the grade of oil

required, either by the specific gravity or (more accurately) by the viscosity.

These oils find application in the paint and varnish industry both in varnishes and in "enamels." The latter term is applied to a type of paint which dries with a glossy surface. When used as an enamel medium, stand oil is open to the objection that it is very much slower drying than even refined linseed oil without driers. The addition of the usual driers to stand oil does not produce the necessary degree of acceleration and, consequently, only a limited amount of stand oil can be used in enamels.

On the other hand, the film produced by stand oil has a very high degree of durability. In practice, therefore, mediums are largely used which also contain China wood oil and sometimes either natural or synthetic resins. In either case it is frequently desirable to use a previously thickened linseed oil in making the enamel medium and this is also the case with the majority of the very important varnishes the composition of which includes China wood oil.

The production of stand oil of consistently high quality is therefore an important part of the varnish maker's work, while as stand oil is frequently used in conjunction with white pigments it is necessary that it should be as pale in colour as possible.

MANUFACTURE OF STAND OILS

The process of manufacture is simple. The linseed oil is heated to the required temperature until the desired degree of thickness is reached. As linseed oil oxidises rapidly at high temperatures it is desirable to exclude air so far as possible, and in some of the plants to be described later the thickening is actually carried out in the presence of carbon dioxide so that oxidation is entirely eliminated. Such plants, however, are complicated and expensive and much stand oil is still made in ordinary oil boiling pots fitted with covers and connected to a good draught, so that the noxious and inflammable fumes are conducted away. In order to avoid discolouration of the oil, considerable attention must be paid to the material of which not only the pot but also the cover and its connection to the draught system are made. The importance of this is often overlooked. The fumes given

off by the hot oil are strongly acid in character and consequently discolouration due to the condensed fumes acting upon the cover and the draught pipe and then falling back into the pot is really a serious point.

As regards the pot itself, such action as occurs between the oil and the metal is practically confined to the surface layer where the oil comes into contact with the air.

These considerations also apply to the manufacture of ordinary varnishes but are of special importance in the case of stand oils on account of the great importance of pale colour in the final product and the length of time at which the oil is maintained at a high temperature.

As regards the oil used, it is important that it should be of high quality and free from mucilaginous matter which would be precipitated at the temperature of heating. If acid refined oil is used it must be free from all trace of mineral acid as this would cause charring and discolouration.

PROCESS AND PLANT

In practice the temperature at which the oil is maintained is about 550° to 570° F. The higher the temperature the shorter the time required to attain the desired viscosity, but on the other hand the danger of darkening the oil is increased. At 570° F. the consistency of the "ex. tint" varnish cited above is reached in about six to eight hours from the time of starting up with cold oil and using about 50 gallons of oil. In estimating the consistency of the finished product allowance must be made for the fact that large batches of oil contained in set pots retain their heat for a long time after the fire is drawn.

In large plants the pots are usually arranged so that the hot oil can be pumped direct to storage tanks and the fresh batch of oil put into the pots while they are still hot from the previous batch.

HEAT EXCHANGERS

A further means of heat economy has recently been introduced, namely, an oil heat exchange. This consists essentially of a chamber well lagged to prevent loss of heat and fitted with baffles. The hot oil from the boiling pot is passed

through this and gives up much of its heat to the materials composing the chamber.

The cold oil forming the next batch is then passed through the chamber and absorbs the heat. In this way the heat contained in the last batch of oil is utilised to pre-heat the following batch. There is also the advantage that, the hot oil being rapidly cooled, it is less liable to oxidation and discolouration and is also the sooner available for handling in the works.

In practice, the temperature of the hot oil is reduced from about 550° to 300° F., the cold oil is raised from about 60° to 250° F. or 300° F., and the time of heating in the pot is reduced to about one half with a corresponding saving of fuel.

HEATING ARRANGEMENTS

The kettles used in the preparation of stand oil, if heated by direct firing, are fixed in brickwork in much the same way as the old-fashioned copper but about 6 to 8 in. are left projecting at the top. The fires are so arranged that the fire doors are outside the building so as to eliminate risk of fire as far as possible in the event of the pot suddenly boiling over. This, however, should not occur if properly refined oil is used and the pot is not over-filled. Generally, filling to about three-quarters capacity is quite safe.

The mouth of the pot is covered with a lid provided with a hole through which the thermometer passes and also a connecting pipe to the draught system. As already stated, most of the reactions which cause discolouration of the oil occur at the surface and in the region of the cover; consequently it is desirable that, whatever be the material used in the construction of the body of the pot, the upper portion and also the lid and the connections to the draught system should be of aluminium or an alloy which will not produce discolouration in contact with the hot oil.

TEMPERATURE CONTROL

As regards temperature control, since a constant temperature must be maintained for some hours the thermometer must be easily read so that a man can, if necessary, keep observation on a number of pots at the same time. A dial reading thermometer is, therefore, to be preferred while,

particularly if the plant is in continuous operation day and night, an automatic temperature recording device is a great advantage. Such arrangement not only enables the manager to keep a close eye on the operation without even leaving his office, but also provides a permanent record of the thermal history of every batch made.

When the oil has been sufficiently heated it is removed from the pot by means of an outlet pipe at the bottom. This outlet should be inside the factory, that is, on the opposite side of the brickwork to the fire door.

BLOWN OILS

Another type of oil which is becoming increasingly important is blown oil. This is prepared by heating the oil and blowing air through it. Under these conditions the oil is thickened and oxidised. The operation is performed in a closed vessel fitted with stirring gear and air pipes. The oil is heated to about 260° F. and air then blown in. Oxidation is so rapid that it is sometimes necessary to cool the plant to prevent over-heating. The temperature is maintained at about 400° F.

As in the case of stand oil, the consistency of the final product can be regulated by adjusting the duration of the process. An increase of weight up to about 10 per cent can be effected and the oil is then so thick that it cannot be poured. The product obtained has good drying properties and the rate of drying can be accelerated by the addition of driers. The chief value of blown oil depends on the flowing properties it imparts to paints and it is largely used in certain types of paint. Its effect on the durability of the film, however, seems to be doubtful.

The oil has a high acid value and cannot, therefore, be used to any extent with basic pigments as it would combine with them, giving brittle and easily destroyed films. On the other hand, with certain inert pigments the film remains sticky, due apparently to the presence of non-drying decomposition products. Although a useful oil, blown oil must therefore be used with caution.

SPECIAL METHODS OF HEAT TREATMENT

Under this heading it is proposed to discuss certain recent developments which present somewhat novel features and

are particularly of interest in the preparation of oils of the type described in this chapter.

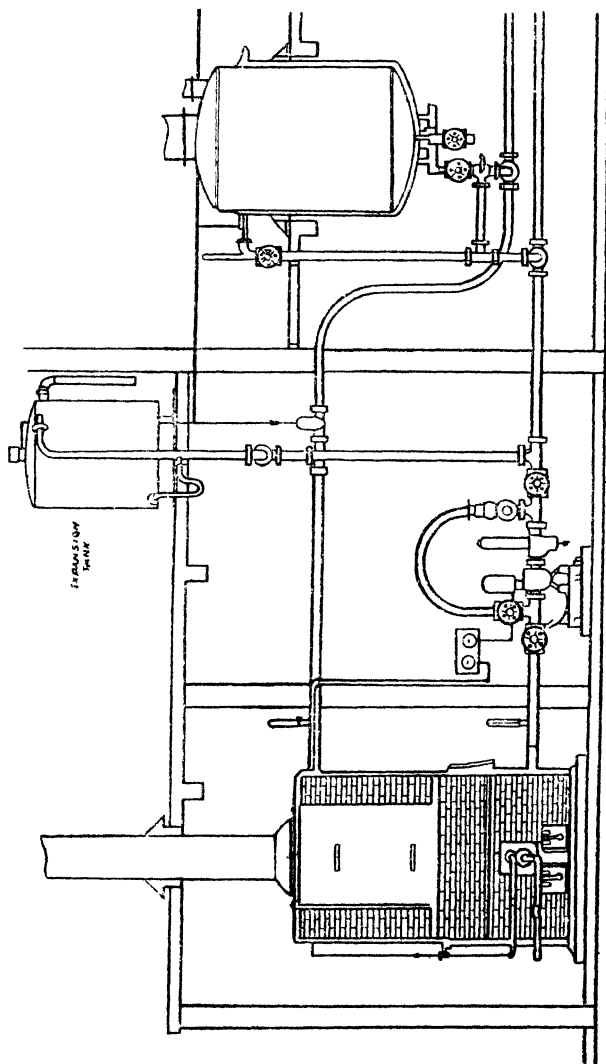


FIG. 1.—Diagrammatic representation of the oil-circulation system.

THE KESTNER MERILENE PROCESS

The danger of fire is ever present in the varnish factory, and, therefore, methods of heating which eliminate proximity

of the fire to the varnish making plant are of great interest apart from other considerations.

The Kestner Merilene system has certain advantages when compared with direct fired pots, whether heated by the direct flame from a coke fire, gas or oil. With this system the varnish pan is either jacketed or fitted with coils, and the heat is applied by circulating special fluid heat transmission oil at a high temperature and a low pressure through the jacket or the coils as the case may be. Fig. 1 shows diagrammatically a typical installation, from which the general principle can readily be seen. The plant consists essentially of the absorber, circulating pump and expansion tank.

The pump is a specially designed positive rotary type, which circulates the heat transmission medium continuously through the absorber and the vessel or vessels being heated. The absorber is mounted in a brick furnace arranged for firing either with fuel oil, gas or solid fuel.

The function of the expansion tank is to allow for expansion and contraction of oil in the system due to variations in the working temperature. The arrangement of piping, valves, etc., forms a patented system, being provided with automatic devices to prevent incorrect operation of the plant; for example, a relief valve is fitted to prevent excessive pressure developing in the system due to the inlet valves in the jackets or coils being closed and an automatic valve also cuts off the supply of fuel oil or gas to the burners in the event of the circulation of the heat transmission fluid failing at any time. An automatic temperature regulator can be arranged so that the contents of the varnish pot may be kept at any desired temperature.

The plant can be operated safely with the temperature of the circulating oil up to 600° F., and in actual practice the pressure of the heat transmission medium in the jackets or coils rarely exceeds 10 to 15 lbs. per sq. in. above atmospheric. The ability to obtain high temperatures without high pressures is a special feature of this system, and has many advantages, both in operation and in construction of the heating pans apart from reduced fire risks.

Rapid heating is obtained but without any local overheating, as the drop in temperature of the heat transmission fluid passing through the jacket or coils of the varnish pot is com-

paratively small—usually about 30° F., so that there is an almost uniform temperature of the whole of the surface, thus preventing deterioration of the product. On the other hand, with direct fired pots the temperature at the bottom is very high, and often very little heat is transmitted through the sides of the pan, so that the intensive local heat may have the effect in time of destroying the metal of the vessel itself.

Accurate temperature control is obtained and owing to the efficiency of the heat insulation, the time required to raise the temperature is very short, and the cooling of the oil in the vessel is correspondingly long, so that, for example, with stand oil, it is possible to turn off the heating long before the desired consistency is reached and to finish the cooking by absorption of the heat in the system.

A number of pots can be operated from the same system, and a large saving in fuel consumption can be obtained by preheating cold oil through a heat exchanger with the finished hot oil.

Apart from the various advantages of the system, working costs are said to compare very favourably with direct firing. The absorber has a much higher efficiency than a pot over an open fire, though the running costs naturally vary widely depending upon the cost of the fuel, the temperature to which the oil is to be heated, and the length of time it is maintained at this temperature. As an example, in the case of a Merilene plant using fuel oil, the oil was bodied at 560 to 570° F. and the consumption of fuel oil corresponded to a cost of $\frac{3}{4}$ d. per gallon of finished bodied oil. This plant replaced an existing direct coke fired installation, and this fuel cost figure compared very favourably with the corresponding cost with coke firing.

In another case where the bodying temperature was lower, being about 550° F. and the time of bodying also shorter, the cost per gallon, using fuel oil, worked out at $\frac{1}{3}$ d. per gallon.

In another case, 300 gallons of oil were heated in the same time, and to the same temperature, using 25 gallons of fuel oil with direct firing compared to the use of 30 to 35 gallons of fuel oil with the Merilene system when heating 360 gallons of oil. It is difficult to make accurate comparison unless exactly the same quantities and similar vessels are used, and an average taken over continued operation for some time.

OIL HEATING

Oil can also be used for direct heating, in which case the consumption of the oil is rather lower than by the oil-circulating system. Too much importance, however, must not be attached to mere fuel costs.

Generally speaking, it is found that so far as gum running is concerned, and in the treatment of linseed oil and China wood oil varnishes, more accurate temperature control is obtained by the use of direct gas firing than by direct oil firing. In selecting a method of heating, the conditions under which varnish is made and the amounts which can be made economically at one time have also to be considered.

The oil-circulating method lends itself particularly to the regular treatment of fairly large batches of oil, whereas gas firing seems to be particularly adapted to those cases such as gum running where careful individual supervision of each batch is of importance.

At the present time methods of heat treatment in varnish manufacture are developing very rapidly, and the whole subject is one in which the manufacturer is well advised to keep closely in touch with new developments.

Electrical Heating Process. The use of electricity has made considerable advance during the last few years in varnish work. One type, the Kestner isoelectric heating plant has been successfully used for the heating and bodying of linseed oil, the principle being indicated in the sketches, figs. 2 and 3.

The vessel containing the oil is constructed in whatever metal is required, and it is provided with internal heating elements specially designed so as to give a large heating surface, and so disposed as to afford efficient thermic circulation of the oil. The vessel is surrounded by lagging with an outer steel casing and the temperature is automatically controlled so that the supply of electricity is cut off when the pre-determined maximum temperature is obtained, the circuit being closed when the temperature has fallen to the required minimum. The maximum and minimum temperatures are readily adjustable, so that the automatic control temperatures can be set for different classes of work.

Even more so than in the case of the Merilene type of plant, the temperature difference between the heating surface and the oil at any moment is comparatively small, as in this case

the heating surface is not controlled to the same extent by the volume of oil in the vessel. The elements operate, therefore, at a very low temperature—well below visual heat, and this

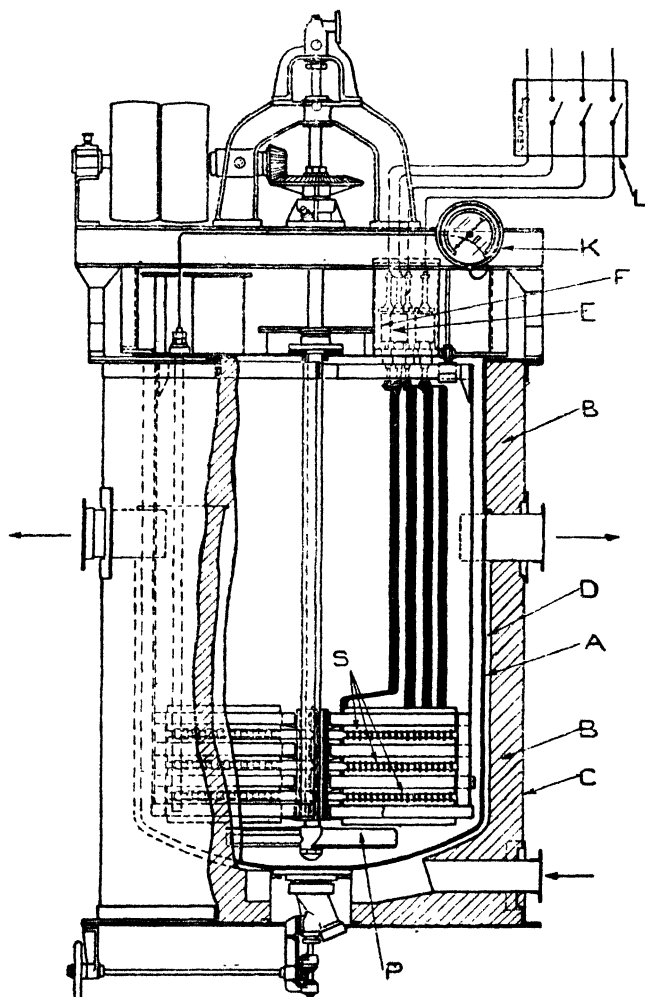


FIG. 2.—The Isoelectric Heating System.

temperature is uniform throughout the whole of the heating surface. The time of heating is rapid, and at the same time local overheating is avoided.

This type of plant is of particular value where special synthetic products are made, in which rapid heating is required under close control, without local overheating. In these cases,

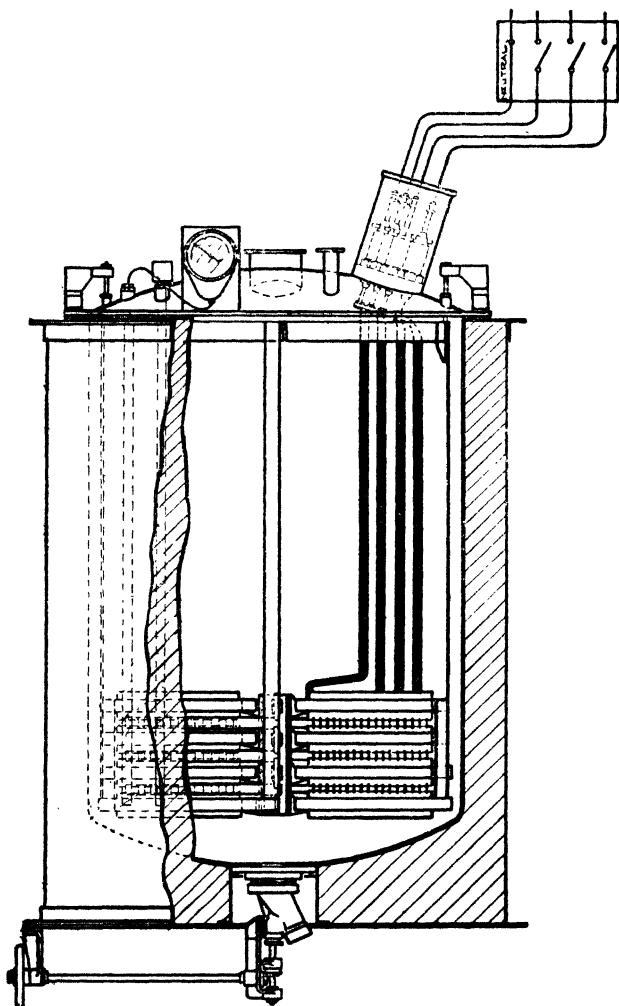


FIG. 3—The Isoelectric Heating System.

a stirrer is often required to incorporate the various ingredients in the reaction, and it is also necessary to have means for cooling in situ and regulation of temperature by cooling as

well as heating. Figs. 2 and 3 show a section of a typical plant of this nature, the principle being similar to the previous illustration with the addition of stirring gear, and also a jacket for controlled cooling by forced air circulation or other suitable means. With this plant oil can be heated to any required temperature, as, for example, 600° F. in about two hours, with charges of several hundred gallons, but without sacrifice of quality of the oil, local overheating being avoided. Apart from reduced fire risks, this system presents the advantages of controlled and quick heating without danger of decomposition and with automatic control. Operating costs naturally depend upon the cost of electricity, but the following figures (which were taken over fourteen months' working of a plant for the production of high grade lithographic varnish) are of interest :

Quantity treated	...	...	210 gallons
Time of heating	...	...	100/110 mins. to 565° F.
Bodding time	...	...	7 to 8 hours
Acid number	...	...	7.6 to 8
Fume loss	...	...	2.3 per cent by weight
Colour	...	...	Lovibond, 35 yellow, 3.4 red
Original colour	...	...	„ 30 „ 3.5 „

The current consumption was about 76 kw.h. per 100 gallons of oil, which with electricity at $\frac{1}{2}d.$ per unit, gives a cost of .38 pence per gallon of oil bodied. It is preferable to work the plant continuously so that part of the heat in the vessel, after completion of a charge, can be utilised for pre-heating the fresh charge, and this will reduce the cost of heating, which could be still further lowered by the use of a heat exchanger between the cold in-coming oil and the finished hot oil.

The actual cost of electricity is not the only item to be considered in comparing methods of heating, but in any case this can usually be obtained at a relatively low figure for a demand of this nature—particularly when the plant is arranged for operating partly during the night. Apart from the automatic controls, time switches can be incorporated for this purpose.

Gas Heating. Great advances have been made during recent years in the application of gas both for oil-boiling and gum-running. The efficiency of gas as a heating agent depends

very largely upon the design of the burner and the furnace. The essential features of a gas furnace are as follows :

The burners are arranged to feed into the combustion chambers so placed that the emergent flames enter the circular hearth tangentially. For a small pot one burner is sufficient but a large pot may have three. Arranged in this way the flames do not play directly upon the bottom of the pot and the heat is very uniformly distributed. The valves are so adjusted that when the gas is turned down the air supply is correspondingly reduced and the heat control is therefore very sensitive.

In the case of the gum-running pots a somewhat different arrangement is found to be most satisfactory, the gas being fed through a multiple jet burner and the flames play directly upon the bottom of the pot. In this way intense local heating is obtained and it is found that, provided the air supplied is properly regulated, there is little or no damage to the bottom of the pot.

CHAPTER IV

CHINA WOOD OIL

CHINA wood oil, or tung oil, is of comparatively recent introduction to the English varnish industry, but it has established itself as an important raw material for the manufacture of varnishes. Its most characteristic property is that on heating it polymerises so rapidly that a few minutes at a temperature of 550° F. are sufficient to convert it to a firm, solid jelly. On exposure to the air the oil dries, giving a wrinkled, "frosted" film.

Polymerisation plays a more important part in the drying of China wood oil than in the case of linseed oil, but drying is accelerated by the same metallic catalysts. The characteristic wrinkling of the film can be prevented by suitable treatment of the oil in the varnish-making process, while the polymerisation on heating can be arrested by the addition of rosin, ester gum and other materials. The oil, therefore, presents many peculiar problems to the varnish maker and must be handled with caution and strict attention to detail. The varnishes produced by properly controlled procedure are, however, extremely useful and possess very high qualities, particularly in the matter of durability and rapid drying. It is therefore very important that the varnish maker should carefully study the oil and methods of using it.

The oil is obtained from trees of the genus *Aleurites*, which are indigenous to China and Japan. Several species of the genus give oils possessing the properties of China wood oil to a greater or a lesser degree, but only two are of importance, *Aleurites Fordii* and *Aleurites Montana*, and there is reason to believe that the oil from the latter species is inferior in quality, though possibly the less careful methods of extracting and preparing the oil for the market may be largely responsible for the inferiority of the oil from the southern portion of China where the tree grows.

The oil from southern China is largely exported through Hong Kong and is therefore known as "Hong Kong oil," while that from the northern area is exported through Hankow and is called "Hankow oil."

From what has been said about the properties of the oil it will be realised that purity and consistency of properties are of first importance, and when the value of the oil to the varnish trade was realised European and American dealers began to take an interest in the supervision and grading of raw material. These activities have been mainly concentrated on Hankow and "first quality Hankow oil" is the standard grade used for varnish making.

The specification of this oil is as follows—(B.E.S.A. Specification No. 391) :

Specific gravity	...	...	...	...	0.939—0.943
Refractive index (20° C.)	...	...	...	...	1.518—1.522
Iodine value	...	...	...	...	155—167
Heat test	...	...	...	...	12 mins. (max.)
Insoluble bromide	...	...	...	...	nil
Acid value	...	...	...	...	5.0 (max.)

No oil which does not conform to this should be accepted for varnish making.

TESTING CHINA WOOD OIL

Of the tests in the above specification the most important are the refractive index and the polymerisation tests. It will be noted that the refractive index is much higher than that of any other vegetable oil while, of course, the polymerisation test is peculiar to this oil. Adulteration or inferior quality are therefore most easily detected by these two tests. The polymerisation test is particularly important and the physical properties of the jelly obtained from the sample should always be carefully compared with those of a standard sample. A standard oil will invariably set in nine minutes under the conditions of test and defective quality is revealed by the condition of the jelly, even if the deficiency is not sufficient to increase the setting time to the maximum limit of twelve minutes.

USE OF CHINA WOOD OIL IN VARNISH MANUFACTURE

From the description of the properties of China wood oil

it will be realised that its use in varnish manufacture requires considerable skill and careful attention. If heating is carried out at too high a temperature or for too long a time the oil may set to a solid leather-like mass in the pot, thus causing great waste of time as well as material. In practice it is usual to arrange matters so that when the China wood oil has been sufficiently heated it may be cooled below the danger point by the addition of a considerable amount of comparatively cold material.

In some cases, as for instance when using rosin or ester gum, it is possible to heat the oil with the resin and thus reduce the rate of setting of the oil. When China wood oil is used with linseed oil it is not advisable to start with a mixture of the raw oils as linseed oil thickens much more slowly than China wood oil. A thickened linseed oil is therefore used. Examples of these various methods of procedure are given in the chapter on varnish manufacture.

If the China wood oil is not sufficiently cooked the varnish is liable to wrinkle or web and for this reason it is used in certain kinds of finishes particularly of the pigmented type to produce wrinkled, crazed and crystalline effects. There appears to be some difference of opinion among varnish makers as to the relative advantage of low temperature and long cooking or high temperature and short cooking. Much depends upon the type of varnish and the conditions prevailing.

Low temperatures certainly are an advantage in that not only is the batch more easily controlled but there is less danger of discolouration. On the other hand, with high temperatures the time of working is much reduced. Generally, it is quite possible to work China wood oil at a temperature of 480° to 500° F. without danger, but over 525° F. setting is very rapid unless rosin or some other restrainer is present. Below 480° F., however, there is considerable danger of the varnish webbing unless heating has been very prolonged. When preparing thickened China wood oil for use in varnishes it is possible to adjust time and temperature within fairly wide limits. Ten hours at 370° F. or four hours at 460° F. may be taken as typical extremes. With large batches of oil it is evident that the maximum temperature compatible with safety is limited by the fact that a large bulk can neither be heated nor cooled so rapidly as a small batch. Polymerisation

occurs fairly rapidly at temperatures over 300° F. and consequently a large bulk of oil may be in a very advanced stage of polymerisation as compared with a small batch heated rapidly to the same temperature. A further consideration in connection with the bodying of China wood oil is that of the amount of thinners required to produce a varnish of working consistency. If the oil is too thick it may require so large a proportion of thinners that the varnish is lacking in gloss. When using the small batches they may be rapidly heated to 530°—535° F. and immediately chilled by the addition of the other ingredients of the varnish.

OTHER VEGETABLE OILS

Linseed oil and China wood oil are the only oils used on a considerable scale in the manufacture of varnishes. It may be of interest, however, to refer briefly to a few oils which occasionally come within the range of the varnish maker, mainly due to the fact that they are sometimes used in paint media. These oils are all inferior to linseed and to China wood oil in drying properties and it will be noted that their successful use is at present confined to a drier and warmer climate than that of Great Britain. It is not impossible, however, that with increased scientific knowledge methods of treatment may be discovered which will render these oils more generally useful to the varnish manufacturer. In any case, the varnish maker is expected to know something about them.

1. *Perilla Oil* is obtained from *Perilla ocumoides* which grows in Manchuria and parts of the East Indies. Recently, experiments have been made with a view to its cultivation in South Russia but the results so far are not definite.

Chemically, it ranks with linseed oil, being highly unsaturated and having an iodine value of about 200 as compared with 190 for linseed oil. In practice, however, it is not very satisfactory for use in varnishes as it does not give a hard coherent film. This is probably connected with the fact that it has a high surface tension and therefore tends to collect into droplets when spread out in a thin film. It is stated that this defect can be overcome by heat treatment and the oil is used to some extent in America. The amount available in this country, however, is small and therefore efforts to utilise it have not been actively pursued.

2. *Poppy Oil* is a slower drying oil than linseed and is used to some extent in artists' colours where its pale colour and slow drying are advantageous. It is obtained from the poppy (*Papaver somniferum*), and with the decline in the opium trade the amount available is comparatively small.

3. *Fish Oils*. The use of fish oils in the preparation of paint media has been actively studied in America and considerable quantities are used. The chief source is the menhaden, which is caught in enormous quantities off the American coast. When properly refined and heat-treated the oil gives a satisfactory film and dries well, but its use in this country has not yet developed to any extent.

4. *Soya Bean Oil* is a semi-drying oil having an iodine value of about 120—130. It is comparatively slow drying and its use in this country is not extensive. It appears, however, that with suitable driers it can be made to dry sufficiently rapidly for use in some climates. It is available in enormous quantities, the soya bean being by far the largest of all the seed crops except cottonseed. Over 6,000,000 tons are estimated to be produced yearly of which about 75 per cent is crushed.

The seeds are obtained from the leguminous plant *Soja max*; this is native to China, Korea and Manchuria, but is also very widely cultivated as, for example, in the United States, which ranks as one of the most important producing countries.

5. *Lumbang Oil* is obtained from a tree, *Aleurites Moluccana*, which is closely related to the tree producing China wood oil. The oil does not, however, possess the property of rapid polymerisation on heating, characteristic of China wood oil, and as regards drying properties is intermediate between linseed oil and soya bean oil. With suitable driers it can apparently be made to dry with reasonable speed in some climates, but experiments made in this country by T. H. Barry (J. Soc. Chem. Ind., 1929, 48; 289) using a formula which was favourably reported upon in the Philippine Islands, gave unsatisfactory results, the paint having very little drying property at all. Evidently this is another example of the influence of climate upon the drying of oils.

6. *Castor Oil*. This oil is obtained from the seeds of *Ricinus communis*, which is grown in India in large quantities. The oil is remarkable in that it contains the glyceride of an

acid, ricinoleic acid, in which one of the hydrogen atoms is replaced by a hydroxyl group. The oil therefore has markedly different properties from the other vegetable oils. From the point of view of the varnish trade the most interesting is its solubility in alcohol. The oil is therefore used in spirit varnishes in order to increase the elasticity of the film. It is used largely for this purpose in the cellulose lacquer industry.

CHAPTER V

THINNERS AND SOLVENTS

THE mixture of oil and resin which constitutes the permanent part of the varnish film is too viscous to be applied by brushing and therefore a proportion of volatile substance ("thinner") is added, the main function of which is to reduce the varnish to a workable consistency. Having fulfilled its duty in this respect, the "thinner" evaporates. It should be noted, however, that the relations between the thinner and the other ingredients of the varnish are not so simple as this statement would seem to imply. The nature of the film depends very largely upon the nature of the solvent and the complex physical changes which occur during the process of evaporation; also small amounts of the thinner remain almost indefinitely in the film and have a considerable influence upon its properties.

It is essential that the thinners be such that at no stage of the drying process will any of the ingredients be precipitated; in other words, the varnish film must remain homogeneous. Apart from the nature of the thinners, the manner in which they are added to the varnish is also important. When the mixture of oils, resins and driers has been cooked it is allowed to cool sufficiently to permit the addition of the thinners without undue loss by evaporation. If the thinners are added too rapidly or without sufficient stirring it will often be found that a heavy precipitate is formed; in fact, in extreme cases a large proportion of the non-volatile ingredients may be precipitated in the form of a stringy mass which will not re-dissolve. This, of course, is simply a convincing demonstration of the fact that a varnish is a complex and very delicately balanced colloidal system and not a simple case of solution. This tendency to separate exists in practically all oil varnishes and though separation on the scale described during the process of thinning may be embarrassing to the responsible party it is really better that it should happen in this somewhat dramatic and obvious way than slowly and unobserved in the cans after dispatch to the customer and the deficiencies or misfortunes of the varnish maker made public.

The selection of thinners, their mode of addition, and the subsequent behaviour of the varnish must therefore be carefully studied, and a satisfactory routine having been devised no departure from it may be permitted. Even if the choice of thinners and the mode of addition have been satisfactory, important changes occur in the varnish for a considerable time after it is made. A certain amount of precipitation occurs and changes in viscosity and drying properties continue for at least a few weeks. The extent and duration of these changes depend largely upon the process of manufacture and the selection of the raw materials (see Varnish Clarification, p. 101). In the case of spirit varnishes, the conditions may perhaps appear simpler and the functions of the volatile ingredients merely as a solvent for the resin predominant, but in reality the same considerations apply as in the case of oil varnishes. It is necessary that the volatile portion of the varnish should be such that a uniform and homogeneous film will remain and that it will possess the requisite degree of hardness and elasticity.

In oil varnish manufacture, turpentine and white spirit are by far the most important thinners, while in spirit varnishes alcohol (methylated spirit) and coal-tar hydrocarbons are the most important. One of the most striking developments of the oil and colour industries has been the introduction of a large number of synthetic organic solvents of various degrees of complexity which have mainly been used in the manufacture of cellulose lacquers. Some of them, however, are used in the preparation of varnishes, though in comparatively small amounts.

TURPENTINE

Turpentine is the oldest of the varnish thinners and still one of the most important. It is the volatile portion of the oleo-resin obtained from various species of pine. By far the largest producer is the United States of America. In Europe, France has a well developed turpentine industry and in a few other countries, notably Spain, the turpentine industry is being energetically developed, while in India the exploitation of the pine forests of the Himalayas is now an important and profitable industry. None of these countries, however, produces enough surplus for export on any considerable scale so that for all

practical purposes we in this country are entirely dependent on the exports of the United States.

At the present time Europe takes about 80 per cent of the American exports. In recent years the total production of U.S.A. has been about 600,000 barrels (one barrel equals 50 gallons) of which about 320,000 were exported.

In both France and the United States the industry has been the subject of careful and systematic study with a view to determining the best methods of tapping the tree so as to obtain the maximum yield of oleo-resin without prematurely killing the tree or destroying its value as timber, and treating the oleo-resin so as to obtain the highest possible grades of turpentine and rosin. In the early days turpentine, rosin and tar obtained from the pine were used mainly in connection with ships and hence the industry was known as the "naval stores" industry, a name which is still used, though now only of historical significance.

The turpentines obtained in the various countries referred to differ somewhat in composition but all consist essentially of closely related chemical compounds known as terpenes.

American turpentine contains about 72 per cent of dextro-pinene and 28 per cent of lævo-pinene, whereas in French turpentine the proportions are practically reversed (lævo-pinene 63 per cent and dextro-pinene 37 per cent). American turpentine has an optical rotation of $+8$ to $+16$, whereas French has an optical rotation of -18 to -40 . Indian turpentine contains about 60 per cent of dextro-pinene and two characteristic terpenes, dextro-carene and longifolene. As these two terpenes boil at a higher temperature, it is necessary in the case of Indian turpentine to remove them by fractional distillation.

For practical purposes the following properties and tests are of importance—(B.E.S.A., X 21, July, 1921) :

Specific gravity (15.5° C.)	...	...	0.86—0.88
Flash point	...	...	Not less than 90° F.
<i>Distillation—</i>			
Initial boiling point	...	...	150° C.
90 per cent distil below	...	...	175° C.
Refractive index (20° C.)	...	...	1.468—1.478
Unpolymerised matter, not more than	...	...	6 per cent
Refractive index of unpolymerised matter, not more than	...	...	1.500

Comparison of these figures with those given for white spirit and other solvents and thinners will show that these tests would certainly reveal any serious adulteration of the sample under test.

USE OF TURPENTINE IN VARNISH MANUFACTURE

Until comparatively recent times turpentine was practically the only thinner used in the preparation of paints and varnishes. It is a good solvent for all vegetable and mineral oils and for varnish resins after they have been "run" and also for a good range of the resins used in making spirit varnishes, such as damar, sandarac, mastic and the softer manilla copals.

One important characteristic is that the compounds of which it is composed are unsaturated and on exposure to air absorb oxygen and polymerise. Turpentine, therefore, in addition to its solvent properties acts as an oxygen carrier to the varnish film and this assists drying. The resinous substance formed during the process, being non-volatile, remains in the film and this improves the elasticity. At the same time its presence also contributes to the stability of the varnish during the last stages of drying and helps to preserve its homogeneous character.

WHITE SPIRIT

White spirit is obtained from mineral oil by fractional distillation. Mineral oil or petroleum occurs in enormous quantities in various parts of the world, the principal oil fields on the American Continents being situated in the United States (Pennsylvania, Virginia and Texas) and in Mexico and Venezuela. Russia, Roumania, Galicia, Persia and Borneo are also large producing countries.

The oils from different localities differ in important respects, but all consist essentially of hydrocarbons. Both aliphatic and aromatic hydrocarbons are present in varying proportions, and as the aromatic hydrocarbons have very different solvent properties for the materials used in varnish manufacture the proportion of those present in the white spirit is a matter of practical importance.

The petroleum from Borneo is particularly rich in aromatic hydrocarbons while that from the Pennsylvanian oil fields consists mainly of paraffins. Of the European oils, Roumanian

yields a grade of white spirit particularly suitable for use in the paint and varnish industry as it is richer in aromatic hydrocarbons than the American but does not possess the peculiar odour of white spirit from the Borneo petroleum. In selecting a grade of white spirit for use in the factory it is, therefore, important to study carefully its solvent properties and to ensure that consistency in this respect is maintained in the deliveries.

The production of petroleum and the manufacture of suitable grades has become an enormous industry. As the crude product contains the whole series of hydrocarbons from gaseous methane (CH_4) to solid paraffins containing thirty or more carbon atoms, the fundamental process is one of fractional distillation.

In America the gaseous constituents are in many cases collected and utilised. Carbon black, which is largely used in the manufacture of printing ink and paint, and also in rubber mixing, is made by the incomplete combustion of the "natural gas." The liquid portion is fractionally distilled and the various products purified to the degree required for their use in industry. The grades may be roughly classified as follows :

Boiling below 0°	Cymogen or rhigoline, used as freezing agents
0° — 150° ...	Petroleum ethers and motor spirits
150° — 200° ...	White spirit
200° — 300° ...	Lamp and burning oils
300° — 360° ...	Fuel oil and lubricating oil
Residue ...	Wax, pitch

In practice the proportion of light oils can be increased by "cracking." The stills are designed in such a way that the vapours are subjected to high temperatures before condensing and thus the higher hydrocarbons are partially broken down into lower and more volatile products. It will be noticed that the paint and varnish industry affords an outlet for the distillate which is too volatile for safe use as a burning oil but not sufficiently so for use as a motor oil.

In addition to hydrocarbons, petroleum usually contains varying amounts of sulphur compounds and these must be eliminated, as apart from their evil smell they yield sulphuric acid on combustion and this has a corrosive action on metals and other material, while from the point of view of the paint trade the presence of sulphur compounds in the thinners may

cause discolouration of lead paints. The standard grades of white spirit are usually free from any appreciable quantity of sulphur but it is advisable to test supplies carefully for sulphur compounds.

For commercial purposes white spirit is classified according to distillation range. Typical grades are as follows :—

	S.G.	BOILING RANGE.	FLASH POINT.
No. 1	0.787	145—200° C.	80° F.
No. 2	0.790	160—200° C.	90° F.
No. 3	0.794	160—210° C.	100° F.

For general purposes a spirit corresponding to No. 2 is satisfactory. A spirit with a lower initial boiling point evaporates rather too rapidly, whilst one with a higher end point will be retained in the film for too long a time. The general character of the distillation curve is, however, equally as important as the initial and final boiling point. At least 80 per cent should distil below 190° C. and at least 97 per cent below 200° C. Some specifications allow a minimum of 90 per cent over at 200° C. but this is in the writer's opinion too low. The all-over point should not be above 205° C. It is understood, of course, that the standard distillation apparatus described in B.E.S.A. 2 D 15 is used. If the chemist uses an apparatus of any other pattern his specification must be modified accordingly.

White spirits are classified in the trade according to their distillation range and flash point, and the manufacturer can obtain any particular "cut" he desires provided he can take a sufficient quantity. The usual fractions separated are 160°—180° C. and 180°—200° C.

CHAPTER VI

NATURAL RESINS

THE natural resins used in varnish manufacture are usually referred to in the trade as "gums." It should be noted, however, that, strictly speaking, gums and resins are sharply distinguished groups of substances. The gums are related to the carbohydrates (sugars) and form viscous solutions with water and are insoluble in organic solvents and in vegetable oil. On burning they decompose completely without melting. The resins, on the other hand, are closely related to the essential oils (terpenes) and are insoluble in water but more or less soluble in organic substances and in vegetable oils. On heating, the resins melt and give off volatile oils of a terpenic nature and the residue is soluble in hot vegetable oils. Some of the softer resins are soluble without decomposition but in no case are the resins in the slightest degree soluble in water.

It will be seen, therefore, that in many respects these two groups of substances are sharply contrasted, resembling each other only in that on exudation from the tree they are in the form of sticky viscous substances, and it is owing to this superficial resemblance that they were originally described by the same name.

For the purpose of varnish manufacture, the resins are usually graded according to hardness and solubility. The resins which are completely soluble in volatile solvents without heating are used in the manufacture of spirit varnishes while the types which have to be "run" are used in the manufacture of oil varnishes. It should be noted, however, that both as regards solubility and hardness there is a practically continuous series from the hardest Zanzibar copals to the softest damars.

As regards chemical composition, the most important ingredients of the resins used for varnish manufacture are complex organic acids and inert substances (resenes) of which

the chemical constitution is very little understood. On heating, the acids decompose to some extent and consequently the acidity of the "run" gum is considerably lower than that of the original substance. The acidity of the finished varnish must therefore always be determined.

As the acids present in natural resins are very complex and their properties very little understood, it is usual to describe the acidity of a resin as equivalent to so many milligrammes of potash per gramme of resin, as in the case of oils and fats. It should be noted that the "acidity" of a resin which is only partially soluble in the solvent used is a somewhat arbitrary figure. The result obtained differs with the solvent used and consequently in order to obtain results of comparative value the conditions under which the test is made must be standardised.

In selecting a resin for varnish manufacture attention has to be paid to the following points :

1. *Cleanness.* As the resins are natural products mainly of tropical origin and collected by untrained natives, they are often contaminated with wood and other debris and consequently require to be graded and cleaned. They are also frequently discoloured by the presence of various impurities and, as the colour of the varnish is largely determined by the cleanness and freedom from colour of the original resin, quality in this respect is a very important factor in assessing the value of a sample of resin.

In practice, resins are usually subjected to a preliminary grading and cleaning in the country of origin, but dealers invariably re-grade and sort the resins as received by them in order to suit the requirements of their customers. As it is naturally much more easy to detect the presence of impurities and discolouration in large pieces of resin, deliveries consisting of large pieces are usually preferred by the varnish maker.

2. *Behaviour on Running.* In the case of the oil varnish resins the gum-running process is the first stage and successful varnish-making depends primarily upon this operation being satisfactorily carried out. During this process the resin froths considerably and loses from 15 to 35 per cent of its weight before it is in a suitable condition for amalgamation with the oil. It is essential, therefore, that the behaviour of the resin during this process should be carefully observed before

large-scale operations are undertaken. Naturally, other things being equal, the resin which loses least weight during the running process is to be preferred.

3. *Stability of the Varnish.* Unless the resin is properly "run" it will not form a stable and permanent mixture with the oil but will be precipitated in the manner which has already been described in dealing with solvents (see p. 39).

4. *Quality of the Film.* Generally speaking, the harder the original resin the harder the varnish film it will form, provided, of course, the tests are carried out under comparable conditions.

SPIRIT VARNISH RESINS

With regard to the resins used in spirit varnish manufacture, these are soluble without preliminary treatment in volatile solvents and the criteria of quality in this case are freedom from insoluble impurities, paleness of colour in the resulting varnish, and the quality of the film which, of course, is assessed according to the particular purpose for which the varnish is required.

INDIVIDUAL RESINS

The resins used in varnish manufacture are invariably designated by the country of origin. At the present time the great bulk of the resins used comes from either the Belgian Congo or the Dutch East Indies.

Congo Copal. The resins from the Belgian Congo are usually described as "Congo copals" and are of the fossil resin type, i.e., they are found buried in the ground a little below the surface. The trees from which these resins are obtained still grow, but practically the whole of the resin exported is collected by the natives in the swampy ground along the banks of the Congo river and its tributaries.

During the last few years there have been great changes in the organisation of the trade and sorting and grading, which was formerly carried out at the collecting stations in the Congo, is now carried out almost entirely in Belgium where the resin is cleaned in specially designed machines by being subjected to a blast of sand. The cleaned resin is then sorted by hand into the various grades according to the colour and size of the pieces.

Congo copal has become what may be described as "the

general utility resin " in the manufacture of oil varnishes from natural resins. It is not so easy to manipulate in the gum-running pot as Kauri copal from New Zealand, but with experience and care it presents no particular difficulties.

EAST INDIA COPALS

In the Dutch East Indies the copals obtained are of much greater variety than those from the Congo and include both oil-soluble and spirit-soluble resins. In this case the trees which produce the resins still grow in enormous numbers and resin is obtained in some parts by systematically tapping them. There is also a large amount of resin found, either buried in the ground or in the forks of old trees, which exuded many years, perhaps even centuries, ago.

The resin exudes from the tree in the form of a thick viscous liquid and after about two months becomes sufficiently hard to be removed from the tree and is then suitable for use in spirit varnish manufacture, being completely soluble in alcohol (methylated spirit). In course of time the resin, if left on the tree, hardens still further until ultimately a resin practically insoluble in alcohol is obtained and which is therefore only suitable for use in the manufacture of oil varnishes.

The resins from this region are usually described as " Manila copals " because originally they were mainly exported from Manila in the Philippine Islands. Since 1916, however, the Dutch have made very vigorous efforts to organise the trade in their East Indian Empire and at the present time the bulk of the resin comes from the Dutch possessions, a large proportion of it being exported from Macassar.

It is becoming more common, therefore, to describe these resins by the names of the various ports of the East Indies from which they come, the most important being :

1. *Macassar Copal*, which is a very fine grade of copal. Macassar is the chief port of Celebes.
2. *Lowoe Copal*, which takes its name from the port of that name on the southern side of the Celebes. There are various grades of the resin and it is characterised by a peculiar odour suggesting mint. The best grades are almost identical with Pontianak copal.
3. *Zambas Copal*, a very fine grade of copal which is exported from Zambas in Pontianak.

4. *Ternate* is the name of a small island in the Celebes group. The resin from this island varies considerably in quality. It is usually very dark on the surface, but some pieces are almost water-white, and a varnish made from it is not so dark as would be expected from the colour of the resin. It is a rather soft grade and some grades are almost completely soluble in alcohol.
5. *Labuan*. A certain amount of copal is exported from Labuan, a port on the southern boundary of Sarawak, in the island of Borneo.
6. *Pontianak*. The resins from Pontianak are used largely in the manufacture of oil varnishes and are of very high quality. The resin has a peculiar odour suggestive of turpentine. Some of it is obtained by tapping the trees and this of course is fairly soluble in alcohol, but the typical grades are of the fossil, or semi-fossil variety and are used in the manufacture of oil varnishes.

The East Indian resins are also sometimes described by the native names for the three principal types. "Melengket" is the native name for the soft, alcohol-soluble grade; "Loba" the name for the medium grade which, although partially soluble in alcohol, is not sufficiently so for use in spirit varnishes; and "Boea" is the hard copal which is either dug up from the ground or found in the branches of old trees. This resin, copal Boea, is practically insoluble in alcohol and is suitable for use in the manufacture of oil varnishes, but the amount appears to be decreasing. It is estimated that about 10 per cent of the output of the Dutch East Indies is "Boea" and 20 per cent "Loba."

"Boea" resins are divided into two classes, the "white Boea" obtained from the branches of trees, which is naturally paler and more free from impurity, and the "brown Boea" which is dug up from the ground and is darker in colour. Very little brown Boea is now obtained.

It will be seen from the above summary that the "Manila copals" cover practically the whole range of varnish resins as regards properties; consequently great care is required in selecting a suitable grade for the manufacture of any particular varnish and it is necessary to test every supply in order to ensure consistency of quality.

In the case of the varieties used in spirit varnishes, the most

important practical test is to make up a solution of the required strength in the solvent to be used and note both the colour of the solution and the amount and nature of the insoluble matter. With regard to the oil varnish type, the colour and size of the pieces, the amount of impurity present, and the behaviour on "running" must be carefully observed.

The varnishes made with the best grade of Manila copal are of good quality but, except with the best grades, the durability is not of the highest order and unless very carefully made the films are lacking in adhesive properties with the result that on exposure it tends to "flay," i.e., come off in strips.

NEW ZEALAND KAURI

This resin is very highly valued in the manufacture of varnishes as it is easy to manipulate and gives varnishes of high elasticity and durability, with a low acid value. A further advantage is that the loss on running is comparatively low. It is, however, rapidly becoming very scarce and consequently the price of good quality Kauri is prohibitive except for very high class varnishes for special purposes.

This resin is produced by the New Zealand Kauri pine, a very large tree which lives to a great age and is highly valued as timber. The resin exudes from wounds in the trunk, but owing to the necessity of preserving the trees, tapping on a commercial scale is prohibited.

The Kauri used in varnish manufacture is fossil resin found buried in the soil in the areas occupied by Kauri pine forests. In the early days enormous pieces weighing several hundred-weights were found, but at the present time only small pieces are found, weighing at the most a pound or two, and even the small chips mixed with soil and debris are carefully sought for.

The resin found varies greatly in quality and is sorted into various grades according to size, hardness and colour.

SIERRA LEONE COPAL

This is a very hard varnish resin obtained by tapping trees which grow in Sierra Leone. In order to prevent the natives tapping the trees to an excessive extent and thus permanently injuring them, it has been found necessary in the British areas to prohibit tapping for two years out of three; consequently

the supply of resin is not very great. In the French area, however, this restriction is not enforced. The total amount of resin exported is not very great—about 150 tons a year—and as the resin is of very high quality it always commands a high price. A small amount of fossil Sierra Leone copal is also found, usually in the beds of streams, but it is not commercially important.

OTHER WEST AFRICAN COPALS

Copal resin is found in many parts of West Africa, but the quality and quantity are very variable. That from Benguela is probably the best and, at the present time, the most important; it is a hard resin and the better grades make excellent varnishes.

The copals from Angola are of two kinds; the red which is very hard and the white which is usually much softer. Red Angola was formerly highly valued, but it is not much used at the present time.

Other West African resins used in varnish manufacture are: Gaboon, Cameroon, Loango, Accra and Benin copals.

Many of these resin fields could doubtless be developed, but the enormous output of the Belgian Congo seems likely to satisfy all demands both as regards quantity and quality for many years to come.

EAST AFRICAN COPALS

The typical resin from East Africa is Zanzibar copal which is the hardest of the natural resins. It derives its name from the Island of Zanzibar from which it was originally exported, but most of the resin is now collected on the mainland, the resin collecting industry having practically ceased to exist on the Island. Before the war the Germans developed the collection of the resin in their territory and exported it mainly through Lindi. The whole area is now included in the Tanganyika Territory under British Mandate. A similar resin is collected on the Island of Madagascar. These copals were formerly highly prized but now are little used, mainly owing to the high price and the fact that by suitable manipulation it has been found possible to meet all normal requirements by the use of the cheaper and more plentiful resins from the Congo area.

SOUTH AMERICAN COPALS

A certain amount of copal comes from South America where there are a number of trees closely related botanically to those producing the East African copals, but the amount at present exported is small and the delivery spasmodic. These resins are known under various names, e.g., Demerara, Para, or Locust gum. South American resins give good varnishes but generally they are distinguished by rather erratic behaviour in the varnish kettle, frequently frothing violently with the result that unless the operator has been forewarned dangerous fires may occur.

ROSIN

Rosin and its derivatives play so important a part in the manufacture of varnishes of all types that it demands special consideration at an early stage in the study of varnish technology. It is therefore dealt with in a separate chapter.

CHAPTER VII

ROSIN

ROSIN (colophony) is an essential raw material in many industries, the largest users being the paper and soap trades, which together take rather more than half the annual world production. The paint and varnish trade probably comes a fairly close third, using about a fifth of the world production.

By far the largest producer is the United States, which is responsible for nearly 70 per cent of the total. France produces about 20 per cent, and the remainder is divided among Spain, Portugal, Greece, India and Mexico. None of these countries has any considerable surplus for export, so that non-producing countries such as Great Britain are practically dependent upon the American product. Great Britain imports about 50,000 tons of rosin a year, of which more than 40,000 tons come from the United States.

The raw material from which rosin and turpentine are obtained is the oleoresin exuded by certain species of pine when the bark is wounded. The composition of this exudation varies with the species of pine and the circumstances attending the tapping of the tree and the collection of the oleoresin. On the average, it contains about 20 per cent of turpentine and 70 per cent of rosin, the remainder being water and extraneous matter.

As the trees are of value quite apart from their resin production, it is important that the tapping operations should be conducted in such a way as to secure the maximum yield of oleoresin without unduly damaging the tree. In this matter France has been the most progressive and far-sighted nation. The French pine forests are situated in the Landes district and are wholly the creation of man. Prior to the plantation of pines the district was unhealthy and unfertile, as the sandy top soil rested upon a waterlogged bed of sand and decayed

vegetable matter. The plantation of pine trees anchored the shifting sands and protected the undergrowth from the heavy Atlantic winds, so that, with the introduction of proper drainage, this district has now become not only healthy but the centre of a valuable industry employing many thousands of people. The methods of exploiting the forests and the system of replanting have been carefully worked out to ensure the maximum permanent production of oleoresin.

In the United States, however, the pine forests are of natural growth ; they originally extended along the whole eastern coast and seemed almost inexhaustible. Careless and wasteful methods of tapping the trees and the enormous increase in the demand for "naval stores" (rosin and turpentine) together with the spread of other industries, led to the wholesale destruction of forests, with the result that the industry is now confined to the southern states, Georgia and Alabama being the principal producers. The export trade is conducted from Savannah and New Orleans.

In France the species of pine cultivated is the maritime pine, *Pinus maritima*. In the United States there are several species which produce oleoresin in sufficient quantity for commercial exploitation, the most important being the long leafed pine *P. palustris*. A full account of the methods of tapping the tree and collecting and distilling the oleoresin cannot be given here ; the reader is referred to the standard works mentioned in the Bibliography (p. 124).

Briefly the process consists in removing the bark from the tree in strips and fastening a vessel below the wound thus made so that the viscous exudation runs into it. The contents of the pot are collected at intervals and, after removal of impurities by sedimentation, subjected to steam distillation. The volatile portion is the turpentine of commerce, and the residue is rosin (colophony). The older stills were direct-fired, water being introduced during the distillation. In the more modern plants elaborate vacuum distillation plants are employed, with consequent improvement in the quality and uniformity of the product. In any case, the rosin is removed from the still whilst liquid and, after it has solidified, is graded according to colour. In order to obtain the palest possible shades the lighter grades of rosin are bleached by exposure to the sun in shallow trays.

In the French system of grading the pale grades are generally called A, the paler the grade the greater the number of A's, AAAAA being the palest commercial grade.

In the United States the grading system is official, and all grading is carried out by an authorised inspector who maintains a set of standards for use as a basis of comparison. The palest grades are WW and WG, medium grades H to M and the dark grades A to G. American rosin is shipped in barrels of 500 lbs. gross (420 lbs. net) weight.

PROPERTIES OF ROSIN.

Rosin is a somewhat brittle solid the colour of which varies from pale yellow to almost black. It becomes sticky with the warmth of the hand and melts at 80° to 90° C. It is completely soluble in alcohol, white spirit, coal tar hydrocarbons, turpentine and most of the industrial organic solvents. It dissolves readily in both vegetable and mineral oils without decomposition and is compatible with practically all the materials used in the varnish industry.

Rosin has therefore a very wide range of application but, from the point of view of varnish manufacture, its use is limited by its softness and lack of durability whilst, owing to its high acidity, it cannot be used in paint media for pigments of a basic character. These defects can be overcome to a certain extent by neutralising the acid with a base such as lime or zinc oxide, or by combining it with an organic alcohol such as glycerol thus forming "ester gum" (see Chap. VIII).

Rosin itself, however, can be used to some extent in conjunction with other resins. In oil varnish manufacture it is used to some extent as a flux to assist the fusion of the harder resins, but this procedure is not to be wholly recommended. In any case, only very small amounts, certainly not more than 5 per cent, should be used in varnishes which have any claim to high durability and water resistance, as the presence of rosin in a varnish causes it to become cloudy in the presence of moisture. In cheap decorative varnishes this objection is not so serious, and large quantities of rosin are used in making finishing coats for articles of temporary value such as toys.

Apart from its action as a flux in the fusion of resins, rosin has a distinct action in increasing the stability of many varnishes. This is particularly marked in the case of spirit

varnishes, and its use is therefore legitimate in cases where stability is a matter of first importance and maximum durability not essential.

In the case of varnishes and media made with coumarone resins the addition of a small amount of rosin is an advantage, for coumarone resin is practically neutral, and therefore the metallic driers, particularly lead, tend to separate; the acidity of the rosin counteracts this.

Used alone as a spirit varnish resin, rosin gives a very weak film which can be powdered merely by rubbing with the finger, whilst on exposure to air the film gradually crumbles due to oxidation.

The status of rosin and its derivatives in oil varnish manufacture was entirely altered by the introduction of China wood oil. When heated alone to a temperature of over 260° C. China wood oil thickens so rapidly that proper control is almost impossible, and therefore the ordinary oil resins cannot be incorporated, as prolonged cooking at high temperatures is necessary to ensure thorough amalgamation. Moreover, untreated or insufficiently heat-treated China wood oil dries with a wrinkled and frosted film. The introduction of rosin or ester gum retards gelation and thus permits of thorough cooking; the resulting varnish dries with a smooth and glossy film which possesses high water-resisting qualities whilst, owing to the toughness imparted by the China wood oil, the comparative softness of the rosin is counteracted.

Still further improvement in varnishes of this type has been effected by the introduction of synthetic resins in which rosin is combined with phenol-formaldehyde or glycerin-phthalic anhydride condensation products. Various other oil-soluble resins of a similar type have been produced in recent years, and new modifications are still appearing at a very rapid rate.

The use of rosin as an ingredient of oil varnishes has, therefore, greatly increased in recent years. Successful manufacture of such varnishes demands great care and the development of special technique, particularly in regard to heat treatment. It is not surprising, therefore, that the earlier accounts of the properties of such varnishes are contradictory and often very unflattering. However, at the present time it may be said without qualification that properly made varnishes containing rosin and rosin derivatives in conjunction

with China wood oil are among the foremost as regards durability and water resistance, while they possess the very important property, from the commercial point of view, of very rapid drying.

In selecting rosin for use in the varnish factory attention must be paid to the questions of colour and stability. Owing to its cheapness rosin is not liable to adulteration but, owing probably to variations in heat treatment during the process of manufacture it sometimes varies in the stability of its solution, i.e., crystallisation or "seeding" sometimes occurs. This appears to be more common with the paler grades. It is particularly marked in the case of alcoholic solutions. The cause of this is not known, but it appears to be associated with the fact that the acidic constituents which form over 90 per cent of the rosin are capable of existing in various physical modifications which differ in solubility and ease of crystallisation.

CHAPTER VIII

ESTERIFIED RESINS AND SYNTHETIC RESINS ESTER GUM

ESTER gum has become an important raw material in the manufacture of varnishes, particularly in conjunction with China wood oil. As already explained (see p. 55), ordinary rosin consists almost entirely of acidic substances and is therefore liable to react upon the pigments with which the varnish may be used. Also rosin gives a very weak film and, generally speaking, is not suitable for use as a varnish resin. Even when used in conjunction with other resins it has a detrimental effect if present in more than a small proportion. In conjunction with wood oil, however, very high quality varnishes may be made with rosin or ester gum as an essential ingredient.

Ester gum is prepared by combining the acid constituents of rosin with glycerol. The product is therefore analogous to a fat in that it is a compound of three molecules of an organic acid with one molecule of glycerol.

In practice it is found that the combination between glycerol and the rosin acid cannot conveniently be carried to completion and usually the final product has an acid value of about 10 to 12 which is of the same order as that of many of the oils used in paints and varnishes and not high enough to produce any undesirable results. Apart from its low acidity, ester gum closely resembles ordinary rosin in general physical properties. As regards solubility the most important change is the reduction of solubility in alcohol, the grades of lowest acid value being nearly insoluble. Owing to its low content of free acid, however, ester gum is much less reactive towards alkalies and metals than ordinary rosin. It is also more resistant to weathering and more plastic.

The manufacture of ester gum is a fairly simple operation, but considerable skill is necessary to obtain the best results. In making the palest grades specially constructed plant, preferably of aluminium, is desirable.

Most varnish makers purchase their ester gum from reliable

firms and this is, in most cases, advisable. It is well, however, to be able to make at least an average quality product in the factory and this can be done in the ordinary varnish pot provided it is fitted with a reflux condenser. This condenser must be arranged so that, although the water produced in the course of the reaction can escape, the glycerol, which boils at a much higher temperature, condenses and flows back to the reaction vessel. Better results can, of course, be obtained using a totally enclosed plant. In any case an aluminium vessel should be used to avoid excessive discolouration.

The rosin is heated gently to remove the water and finally raised to a temperature of about 500° F. Glycerol is added slowly and the mass maintained at this temperature until the reaction is complete. Completion is indicated by the melt becoming perfectly clear and a drop on cooling showing no signs of cloudiness due to separation of glycerol.

The amount of glycerol required varies with the degree of neutralisation required and the efficiency of the condensing system in preventing loss of glycerol. From 10—25 per cent calculated on the weight of rosin taken may be required, according to the circumstances.

HARDENED ROSIN

The acidity of rosin can also be neutralised by direct combination with metallic oxides, of which zinc oxide and lime are the chief. Lime hardened rosin is largely used in the preparation of cheap gloss media some of which consist of little more than lime hardened rosin dissolved in white spirit with as little linseed oil as possible to give elasticity.

Such media give very quick hard drying enamel like paints but, of course, have very limited durability.

Lime hardened rosin is also used in certain types of varnish, but generally ester gum is to be preferred.

Combination of the lime with the rosin is effected by heating the rosin to about 450° F. and adding slowly the finely powdered lime with constant stirring. Usually about 8 to 10 per cent by lime is added and the acid value of the finished product is about 10 to 15. It is important that the lime should be pure and particularly that it should be free from magnesia which gives very hard and insoluble soaps.

COPAL ESTERS

Other resins such as Manila and Congo copals, which contain a high percentage of resin acids, can also be esterified but the operation is much more difficult and, therefore, these "copal esters" are invariably prepared by firms specialising in such processes. Like ester gum, these products have the advantage by very low acidity. They also possess the important advantage of dissolving in linseed and in wood oil mixtures at a much lower temperature than the natural resins and not requiring to be "run." There is thus a saving of about 25 per cent by weight. They are also soluble in turpentine, white spirit and in coal-tar hydrocarbons without heating, but are not soluble in methylated spirit or in acetone. The acid value is of the order of 10 to 15 in the case of the Congo esters.

As typical varnishes of this group the following formulæ may be quoted (by courtesy of Messrs. Fred. Boehm, Ltd.):

1. *Mixing varnish.*

100 lbs. Congo ester

166 „ enamel oil

heat to 260° to 280° C. until the resin is completely dissolved; then add

1½ lbs. 6 per cent cobalt linoleate

cool to 180° C.; then add

170 lbs. of a mixture of equal parts turpentine and white spirit

2. *Outside varnish.*

100 lbs. Congo ester

200 „ stand oil

250 „ thinners

2 „ 6 per cent cobalt linoleate

The procedure is the same as in the case of the mixing varnish (Formula 1).

SYNTHETIC RESINS

An important development in the varnish trade during recent years has been the production of oil-soluble synthetic resins. Activity in this direction is still very marked and new products are being produced in great numbers.

The most successful of these synthetic resins, with the exception of those of the coumarone type, depend for their utilisation on the fact that condensation products such as those obtained by combining phenols with formaldehyde or phthalic acid with glycerol can be further combined with

acidic resins to give resinous products which are oil-soluble. A great variety of these is now on the market and varnishes made with them have proved to possess many valuable properties.

Phenol Formaldehyde Type. The resins produced by combining phenols with formaldehyde are generally known as Bakelite resins. The process of combination between phenol and formaldehyde occurs in three stages the products being generally known as A, B and C respectively.

- A. Production of a soluble fusible mass
- B. A solid insoluble mass which softens on heating
- C. An insoluble infusible substance

The transition through these changes is gradual and is effected by heat; usually temperatures of the order of 150° to 200° C. are employed. It is upon this property of thermal hardening that the use of Bakelite resins in mouldings depends.

Such products, however, obviously cannot be used in varnish manufacture except to a limited extent in spirit stoving varnishes in which the heat treatment at once evaporates the solvent and converts the resin to the insoluble infusible "C" form. It has been found, however, that by combining the phenol formaldehyde product with rosin or other acidic resins an oil soluble product can be obtained. The process presents many technical difficulties and is capable of numerous modifications giving a great variety of products.

The albertol resins are of this class and the makers of them have published very elaborate details as to the use of their products in varnish manufacture.

The most important of these resins from the oil varnish manufacturer's point of view are albertol 111L and albertol 209L. The former is more readily soluble in linseed and in China wood oil mixtures than the latter, which requires to be cooked with the oil at about 460° to 500° F. until a sample taken from the varnish pot remains clear when cooled and diluted with twice the proportion of thinner it is intended to use in the final varnish.

These resins are generally used in conjunction with China wood oil and a great variety of varnishes and enamel media can be produced.

Like the ester gums, the albertols are of low acidity and do

not require to be run before they can be dissolved in the oil. Their use therefore eliminates to a large extent the personal factor in varnish making which thus becomes amenable to the mass production methods essential in modern industry.

As examples of the use of albertol resins the following may be quoted. It should be noted that a great variety of formulæ has been devised, over 200 having been published by the makers of these resins alone. The differences largely consist in the heat treatment of the oils and the resin-oil mixture. As already pointed out, this is a fundamental part of the whole process and great attention must be paid to accuracy and consistency in the method of procedure.

1. *Enamel varnish with 111L.*

160 lbs. stand oil

40 „ thickened China wood oil

heat to 300° F. and then add

100 lbs. albertol 111L

The resin is added gradually, and when all dissolved, add

7.5 lbs. of 2 per cent cobalt resinate

When the temperature has fallen to 250° F. add

125—175 lbs. of thinners

The thinners used depend, to a large extent, upon the choice of the varnish maker. White spirit is quite satisfactory, but the presence of a certain proportion of turpentine is a distinct advantage, from 5 to 10 per cent being sufficient to aid the drying.

2. *Enamel varnish using 209L.*

In this case a certain amount of cooking is necessary to ensure a stable union between the albertol and the oil.

100 lbs. varnish linseed oil

Heat to 350° F. and add slowly

100 lbs. albertol 209L

When all the resin is dissolved the temperature is raised to 480° F. and maintained there until a small sample from the pot can be cooled down and thinned with double the proportion of thinner to be used in the varnish without it becoming cloudy. When this state is reached, add

200 lbs. stand oil

The temperature is again raised to 420° F. and maintained there till a sample passes the dilution test already described. The batch is then removed from the fire and

15 lbs. 2 per cent cobalt resinate added

followed by

200—300 lbs. thinners

As in the previous case the thinners may be turpentine, white spirit or a mixture of these.

Phthalic Anhydride Glycerol Type. This type of resin, which is generally called the "Glyptal type," resembles the Bakelite resins in that it is produced in three stages A, B

and C. The resin, however, is transparent and almost water-white. As in the case of Bakelite, these resins can be used in the production of certain kinds of spirit varnishes and by further combination with resins or oils can be converted to oil soluble resins which can be used in varnish manufacture.

These resins have not yet been so widely used as the Albertol type but they certainly give varnishes with very useful properties and the makers have published very full details of the way in which to use them.

As examples of this type of varnish the following may be quoted :

Outside varnish.

100 lbs. beccacite (oil-soluble glyptal)

230 „ stand oil

65 „ China wood oil

Heat to 428° F. and then add

1½ lbs. litharge

Raise the temperature to 464° F. until the mixture is perfectly clear, then add

130 lbs. stand oil

and heat at 446° F. till clear. Cool to 380° F. and add

200 lbs. thinners in which is dissolved

16 lbs. 1 per cent cobalt linoleate (or resinates)

Any of the usual thinners may be used—white spirit, turpentine or naphtha.

Coumarone Type. This group of resins is in many ways quite distinct both from the natural resins and the synthetic resins already described.

They are produced by the polymerisation of two substances, coumarone and indene, which occur in the fraction of coal-tar distillate boiling between 160° and 180° C. When treated with sulphuric acid in the presence of a suitable catalyst these colourless liquids polymerise forming a series of products, the final stage being a solid resin which softens at about 80° C. and melts at about 120° C. A complete range of products can therefore be obtained by suitably controlling the polymerising process. The colour can also be controlled by special methods, the palest forms of the harder coumarone resin being as pale as W W grade rosin.

Coumarone and indene resins therefore differ from all the resins so far described. They are perfectly neutral and inert, and are not convertible by heat treatment to an insoluble form. They are completely soluble in linseed and wood oil mixtures,

and in coal-tar hydrocarbons (solvent naphtha). They are less soluble in white spirit and in mineral oils generally, but the addition of about 10 per cent of aromatic hydrocarbon will usually effect solution. In certain grades of white spirit, containing a high proportion of aromatics, coumarone resins will dissolve quite satisfactorily. It should be noted that, being quite inert, coumarone resins do not combine with the other ingredients of the varnish. This necessitates very careful adjustment of the varnish formula so that nothing incompatible with them shall cause precipitation; also the varnish must be well cooked so as to insure that perfect amalgamation takes place. When driers are present it is essential that there should be enough acid, either in the form of resin or oil, to keep the metals in solution as the coumarone resin obviously cannot function in this manner. The complete inertness of coumarone is, however, a valuable property, especially in conjunction with China wood oil as it permits of the manufacture of varnishes which give films of very high resistance both to water and to chemical action generally. Spirit varnishes can also be made with coumarone but, generally speaking, they do not appear to have any extended scope. The films are not very strong but, owing to the complete chemical inertness of the resin, spirit varnishes containing coumarone have some application in the preparation of chemically resistant coatings for special purposes.

As examples of varnishes made with coumarone resins the following may be quoted as typical:

1. *Short oil varnish.*

100 lbs. China wood oil

Heat to 470° F. and add

75 lbs. coumarone (pale varnish grade)

Raise the temperature to 570° F. and withdraw from fire, heating again cautiously if necessary until a drop of the mixture on cooling sets to a hard button. Then add

25 lbs. coumarone resin

and heat at 510° F. till the button obtained on cooling a drop is clear and hard (from 15—30 mins. are required). Remove the pot from the fire and add

1 lb. of 2 per cent cobalt resinate.

Cool to 420° F. and thin with

180 lbs. white spirit

It is desirable that the white spirit should have a fairly high aromatic content. If necessary about 5 to 10 per cent solvent naphtha can be added.

2. *Long oil varnish.*

160 lbs. China wood oil

20 „ coumarone.

Heat to 530° F. and remove from fire. When a drop of the mixture strings on cooling add

50 lbs. linseed oil

followed by

100 lbs. coumarone resin (varnish grade)

Heat to 510° F. for about 30 mins., cool to 350° F. and add

4 lbs. 2 per cent cobalt resinate

300 lbs. white spirit

3. *Medium oil varnish.*

20 lbs. China wood oil

Heat to 470° F. and add

75 lbs. coumarone resin

Stir well; the resin should melt in about 12 mins. Raise the temperature to 535° F., remove from fire, and hold till a drop sets to a fairly hard button. The varnish must *not* string from the stirrer. Then add

25 lbs. coumarone, *followed immediately by*

20 „ linseed oil

Heat to 480° F. till the required body is obtained. Remove from the fire and add

1½ lbs. 2 per cent cobalt linoleate

Cool to 420° F. and then thin with

200 lbs. white spirit

To make a quicker drying varnish add

2 lbs. lead linoleate or resinate to the above driers.

Other Types of Synthetic Resins. The above are the three types of synthetic resins which have so far established for themselves a definite place in the manufacture of drying oil varnishes. Their successful application depends not a little upon the correct heat treatment of the oils (invariably a mixture of linseed and China wood oil) both before and after the incorporation of the resin, and for this reason very careful observation and testing are essential in making up a varnish with these products. It is also essential that when the making of such a varnish becomes a routine factory operation the process should be strictly controlled in every detail, particularly as regards temperature and times of heating. It will also be noted that apart from the coumarone resins, these substances contain natural resins and should, strictly speaking, be termed modified synthetic resins. Recently, new types have been introduced which are wholly synthetic. In some of these the synthetic condensation product, e.g., a glyptal resin, is combined with oil instead of resin, while in the case of the Bakelite type it has been found possible to produce an oil-soluble

type by modifying the condensation process and using different phenols. The higher phenols, such as xlenol for example, yield an oil soluble product when condensed with formaldehyde under suitable conditions. Other methylene compounds than formaldehyde may also be used. The preparation of these and the production of varnishes from them is, however, a highly technical process and has not yet become sufficiently standardized to be incorporated into the general scheme of the varnish maker's operations (see H. H. Morgan, Bibliography.)

CHAPTER IX

SPIRIT VARNISH RESINS

THE resins in this group are soluble without further treatment in various volatile organic liquids, and the solution on evaporation leaves a film usually much softer and less durable than that given by oil varnishes, but very suitable for many decorative purposes. Used in the restricted sense, the term "spirit varnishes" is applied to alcoholic solutions of resins such as the soft Manila copals and shellac, but for the present purposes it is used in the wider sense to include varnishes in which other solvent and resins are used, but which like the alcoholic varnishes dry by evaporation only.

I. DAMARS

The damars are soft resins soluble in coal-tar hydrocarbons—benzene, toluene, naphtha and so forth—petroleum hydrocarbons (white spirit) and in turpentine. These resins are obtained mainly from trees growing in the islands of the East Indian Archipelago, principally in Sumatra and Borneo, and smaller amounts are also obtained from the mainland, principally the Malayan Peninsula and from Siam. Like the copals, the damars are generally described by the name of the port from which they are exported: Mata, Balano, etc. The principal are:

Batavia. Very good grades of damar are exported from Batavia; most of it comes from Sumatra.

Pedang. The damar known by this name comes mainly from Sumatra.

Singapore. Damar from all parts accumulates at Singapore. The quality varies considerably, but generally it is not so high as that from Batavia.

Properties. The chief constituent of damar is an inert substance (resene) which is present to the extent of about 60 per cent. The resins are therefore resistant to chemical

action but owing to their softness cannot be used where exposed to weather and severe wear and tear.

Their use appears to be decreasing. The varnishes made by dissolving damar in turpentine and other solvents are used in making paper varnishes and varnishes for toys and other purposes where durability is not important. One of the drawbacks to damar varnishes is that they always retain a slight stickiness.

The solutions in coal-tar hydrocarbons are clear but in turpentine usually somewhat opalescent, while in white spirit the solubility varies greatly with the type of damar but usually becomes cloudy on standing. In this respect the Batavian damars are the best, whereas the Singapore damars invariably give a considerable amount of white gummy precipitate and sometimes the varnish becomes opaque and almost semi-solid. The addition of resin reduces this tendency but at the same time still further reduces the durability and by increasing the acidity renders the film more vulnerable to chemical action.

Damar has been found to be a valuable addition to cellulose lacquers, but for this purpose it is necessary to remove the portion which is liable to precipitate from the solution. This is effected by dissolving the resin in coal tar or other solvents, particularly ethyl acetate, and then adding wood naphtha (methyl alcohol) which precipitates the "wax" as it is termed. After settling, the clear solution is run off. Most cellulose lacquer makers "de-wax" their damar themselves but a certain amount of business is being done in "de-waxed" damars, though, of course, this involves the introduction of another process, namely, evaporating the solvent in order to obtain the "de-waxed" resin. As the cellulose-lacquer maker promptly re-dissolves the damar in its own solvent, this does not appear to be a very economical process unless some special use, on a large scale, can be obtained for the precipitated "wax."

Damar solutions are also used in conjunction with oil media in the production of enamel media and in anti fouling paints.

Tests. In selecting damar the varnish maker has to consider mainly colour, cleanliness and solubility. As with other resins, large clear pieces free from dirt and dust are preferred, where the varnish has to be filtered and in any case is made

without heating ; the presence of a moderate amount of dirt does not seem important provided the saving in price is sufficient to justify its use but it has to be remembered that in addition to the impurity a considerable amount of solvent is usually lost, partly by evaporation but mainly admixed with the insoluble matter. It is doubtful whether in the long run the use of low grade damar even at correspondingly low price ever pays in the manufacture of spirit varnishes.

In the case of cheap preparations such as anti-fouling compounds when colour and purity are unimportant, one can of course use inferior grades.

Damar Batu—Black Damar. The resins included under this name, although called damar are very different from the transparent grades used in spirit varnishes. They are of very mixed composition, including dark coloured resins exuded from various trees and collected more or less haphazard by the natives, some from the living trees and some from the ground. They are not completely soluble in the usual solvents and are incorporated by fusion into the composition used mainly in treating ships' bottoms.

In selecting them, attention must be paid to uniformity and hardness. The best grade damar Hitam is distinguished by a coating of greyish dust and has a brilliant fracture. Another softer grade, damar Senggi, has no coating of dust, and although the fracture is brilliant, it has a characteristic reddish tint by transmitted light. In addition to these there are a number of resins, sometimes called "bastard copals," varying from a light stone colour to dark brown and of very varied composition, which are used to some extent in cheap preparations.

2. MANILA COPALS

The general properties of these have already been described. The deliveries must be carefully tested for insolubility, viscosity and stability of solution and colour.

3. SHELLAC

Shellac is the product of insect activity. The lac insect breeds on various species of tree which grow in India and in Assam and Indo China. The cultivation of the insect and the manufacture of shellac is, however, practically confined to

India, over 95 per cent of the supplies coming from that country. The collection of the lac and its conversion to shellac is almost entirely a village industry and supplies eventually accumulate at Calcutta for export. In the varnish trade lac is used almost solely in the form of shellac but the possibility of eliminating at least some of the native processes is being seriously considered, and during recent years shellac made by mechanical processes has become commercially successful.

The following brief summary of the production and manufacture of shellac will be sufficient to enable the reader to appreciate the value of the various grades of lac and the names by which they are known.

1. *Sticklac*. When a new brood of insects is settled on a tree, each insect fixes itself to the bark and remains stationary, drawing substance from the tree and excreting the resin which ultimately completely covers the insect. The male insects in due course emerge from their cells but the female remain stationary and after the birth of the new brood, dies. The twigs and branches of the tree are thus left coated with masses of resin and, the new brood having been transferred to fresh branches, they are removed. This is sticklac. The life cycle of the insect is about six months, four crops are obtained every year :

Baisakhi—collected in April and May

Jethwi—from Kusum trees, collected in May and June

Rangeen—collected in October and November

Kusmi—from Kusum, collected in November and December

The lac produced at each crop differs somewhat in properties and the shellac made from a specific crop is often called by that name.

Sticklac is exported to some extent for treatment in European factories, but the great bulk of it is treated in India by the natives. By a long process of sifting and winnowing, washing and drying the sticklac is freed from practically all wood and debris and most of the dye, leaving the lac in the form of granules known as seed lac. Seed lac is used to an increasing extent but so far varnish makers have found that shellac is more satisfactory for varnish making.

The conversion of seed lac to shellac is a remarkable native process which appears to have been used with little or no alteration for many hundreds of years. A mixture of various

grades of seed lac and a certain proportion of rosin and powdered orpiment is put into a long bag, one end of which is twisted as the bag slowly travels in front of a fire. Under the influence of heat the contents fuse and are squeezed out. The resinous mass is skilfully transferred to the outer surface of a jar containing hot water and plastered out into a sheet which is then stretched in front of the fire. The sheet is then broken up, forming the well-known flakes sold as shellac.

Button Lac. Instead of stretching the plastic lac into sheets it may be allowed to fall on a cool surface and then pressed out into a flat circular cake which is stamped with the trade mark of the maker. This is sold as "button lac."

The nature and quality of the shellac varies, of course, with the ingredients and the following are the chief grades :

SHELLACS

1. "Lemon" or "superfine," made mainly from best Kusmi lac.
2. "Fine" and "standard 1," made mainly from best Baisakhi.
3. T.N., made mainly from Baisakhi. In recent years Pegu (Burmese) and Siamese sticklacs have also been used.

BUTTON LACS

1. Pure button lac from the best grade sticklac.
2. Other button lacs. Those made from kiri, molamma, etc., are now practically obsolete.

In practice it is important that the amount of rosin present in the shellac should be known, and this is usually specified in the contract. On the London market the standard grade is T.N., which is specified by the London Shellac Users' Association as being equal in all respects to the official standard sample and to contain not more than 3 per cent rosin as determined by their official analyst.

MECHANICALLY MADE LACS

Various mechanical and physical processes have been developed in India and in Germany to replace the native method. Lacs made by these processes are sold under the trade marks of the makers and are of guaranteed composition.

A complete list of these grades would be very lengthy as

they are made specially to suit the requirements of various industries, but as typical members of the series the following may be mentioned :

Garnet Lacs. These have a characteristic rich garnet colour and the rosin and wax content varies according to the purpose for which the lac is to be used. In the varnish trade, "A. C. Garnet" lac which contains about $1\frac{1}{2}$ per cent of wax and $2\frac{1}{2}$ per cent of rosin is largely used. A purer grade known as "C. Pure" which contains no rosin and $2\frac{1}{2}$ per cent of wax is now being used to an increasing extent though its particular application is in the gramophone industry.

Of the shellacs a whole series containing from 0 to 3 per cent rosin is made to correspond with the native T.N. shellac, from which, of course, they differ in being completely free from dirt.

The above grades are made in India by Messrs. Angelo Brothers, Ltd.

Of those made in Germany by Messrs. Zipperling, Kessler & Co., the two most interesting are probably "ZTN One" and "Double Sun." "ZTN One" is free from rosin and de-waxed ; it is of very low viscosity and therefore specially suitable for use in spraying preparations. "Double Sun" is de-waxed and very pale and designed to compromise between the paleness of a bleached shellac and the mechanical strength of an unbleached shellac.

It will be observed that colour and rosin content are the chief points to which attention is paid. For most purposes the varnish maker will be satisfied with "Standard T.N." but for certain purposes it may be advisable to use some of the paler grades.

4. OTHER RESINS

Of the other spirit varnish resins only comparatively small amounts are used ; the principal are sandarac, mastic and accroides.

Sandarac. Sandarac is obtained from three regions, North Africa, South Africa and Australia. The trees producing it are *coniferae* (Pines). This group of tree has been exhaustively studied by R. T. Baker and H. C. Smith ("A Research on the Pines of Australia Technical Educational series No. 16, Technological Museum, Sydney, N.S.W."), with special reference

to the species growing in Australia. These authors classify the species as follows :

South Africa
North Africa
Australia

Widdringtonia
Tetraclinis
Callitris

The Australia group contains several species of which two, *C. glauca* and *C. calcarate* probably supply the bulk of the Australian sandarac. Most of the sandarac, however, still comes from North Africa and is exported from Mogador. It is, therefore, frequently called Mogador sandarac.

The resin exudes from the trunk of the tree in the form of small transparent tears which rapidly become opaque. The resin which falls to the ground, and thus becomes contaminated with debris and dirt is collected separately and sold as a lower grade.

Sandarac is distinguished from mastic by the fact that it can be powdered between the teeth, whereas mastic softens. On ignition it burns with a characteristic odour. Although harder than mastic sandarac must be counted a soft resin. Its solubility varies considerably but it is generally used with either alcohol or turpentine as a solvent. The film is rather brittle and therefore a plasticiser must be used. In turpentine varnishes, Venice turpentine or elemi can be used, while in alcohol, camphor may be used as well. The varnishes made with sandarac give white and fairly hard films and are used for leather and paper coating and also for wood and metal varnishes.

Mastic. This resin is comparatively expensive and little is used for commercial purposes. It is used mainly in preparing high grade picture varnishes for which purpose it is particularly suited as the film can be removed easily without injury to the painting. In cheaper varnishes mastic is used in conjunction with sandarac, or, if turpentine be the solvent, damar. The film given by mastic varnish is softer and more elastic than that given by sandarac varnishes.

Accroides or acaroid resin, is of two kinds, yellow and red. It is soluble in alcohol, giving a solution which somewhat resembles that of shellac without, of course, the turbidity due to the shellac wax. The film, however, is weak and possesses little of the characteristic toughness and durability of the

shellac film. Accroides, therefore, is only to be used in the cheaper varnishes and its presence in pure shellac varnish must be regarded as dangerous adulteration. Gum accroides is obtained from various trees of the genus *Xanthorrhœa* which grow in Australia. These trees are known as "black boy," "grass trees" or "yacca." The trunk is of a soft spongy nature and the stiff rush-like leaves grow out all round it. As the tree increases in height the lower leaves die off and the resin is found round the stiff leaf bases which remain and form a sort of jacket round the trunk. If, as frequently happens, the tree is fired the resin congeals and the leaf bases blacken. The resin is removed by beating the tree when the brittle resin and some of the leaf bases fall to the ground. In the old days, a rough separation of the resin was effected by melting out the resin producing blocks of "black boy" resin, but at the present time the resin is separated by sifting and winnowing. The resin is used in various types of varnish and numerous other uses have been suggested from time to time. For example, it can be used in paper sizing and in sealing wax, while during the war it was used as a source of picric acid. Varnishes made with accroides are stated to be very sensitive to water while metal lacquers made with the red variety darken rapidly on stoving. Accroides is insoluble in benzol and in petrol and is therefore suitable for use in varnishes and protective coatings which are to be exposed to the action of these liquids.

Dragon's Blood. The use of this resin has almost ceased, as the characteristic red colour which it imparts to varnishes and stains can be more easily produced by the use of soluble synthetic dyes added to varnishes made with other resins. The original dragon's blood resin came from Western Asia, and the best still comes from the island of Socotra. A similar resin obtained from various climbing rātans growing in Malaya is also used under the name dragon's blood. In addition various trees growing in different parts of the world yield red resinous exudations and these appear on the market under the name, "gum kino." Of these West African kino and Australian kino are typical. All these resins were credited with medicinal properties and Australian kino is still included in the pharmacopœia. They are, however, of little industrial importance at the present time.

Colophony (Rosin). Colophony is also used largely in many types of spirit varnish, being cheap and readily soluble in all the usual solvents. Of itself it is not at all satisfactory, the film being very weak and easily affected by water and by alkalies. Within limits, however, its use is quite justifiable. Apart from its cheapness, rosin possesses the property of improving the solubility of some resins, as for instance damar in white spirit. Rosin, however, enters into so many branches of varnish manufacture that it is dealt with in a separate chapter.

CHAPTER X

ASPHALTS, BITUMENS AND PITCHES

THE terms asphalt, bitumen and pitch cover a great variety of substances both natural and artificial which are used for a great variety of purposes. As in the case of the terms oil, resin and wax, the words asphalt, bitumen and pitch, when used in the popular sense, denote a class of substances possessing at least superficial similarity in physical and chemical properties irrespective of their origin and chemical constitution.

The substances included in this group are dark in colour and vary in consistency from soft plastic masses to hard brittle solids. They are of indefinite melting point and vary greatly in solubility in various solvents. Many attempts have been made to evolve a satisfactory classification taking into account both origin and chemical constitution, but in any such schemes there is, as in the case of the natural resins, no precise borderline between the various groups. A review of these schemes of classification is given by H. M. Langton ("Blacks and Pitches," p. 67 *et seq.*, Benn, London, 1928) which includes a very complete bibliography of the subject and to which the reader is referred.

For the purposes of the present work the following abbreviated classification may be adopted as covering the substances of most interest to the varnish maker.

1. PRODUCTS OF NATURAL ORIGIN.

Bituminous substances are found in various parts of the world. They may be described as "alteration products" of petroleum and are found in varying degrees of purity and hardness. They may be divided into three groups.

(a) *Veins of Pure Hard Bitumens usually found in Vertical Fissures of Rocks.* The most important deposit of this character is Gilsonite which is found in the State of Utah, U.S.A., in seams running in almost parallel lines across the country for a distance

of nearly 40 miles, the depth of the seam varying from a few to several hundred feet. This bitumen is in a very pure state and is mined on a very large scale. The best grades contain less than 1 per cent of mineral matter and less than 2 per cent of volatile matter. Gilsonite is a hard substance with a brilliant black conchoidal fracture and gives a brown streak when rubbed on paper.

A number of similar deposits are found in America, an important one being the deposit of Grahamite in Oklahoma. Grahamite differs from Gilsonite in that it gives a black streak on paper, is more dense and of a higher melting point.

A third variety, Impsonite, is found in various parts of the world and may be regarded as the final stage of hardness and infusibility. In this country it occurs to some extent in Derbyshire and is known as Elaterite.

A very hard black bitumen is also mined in Barbados and in Trinidad and sold under the name Manjak. The Barbados variety is largely used in the United States of America in the manufacture of special insulating varnishes and is remarkable for the high proportion of oil which can be blended with it and the elasticity and hardness of the films resulting therefrom.

(b) *Natural Accumulations of Bitumen in "Lakes."* These are of various sizes, by far the most important being the great asphalt lake of Trinidad which covers an area of about 150 acres and is estimated to be about 150 feet deep in the centre. A unique feature of this deposit is the presence of clay and water emulsified with the bitumen. This necessitates a certain amount of refining. The crude bitumen is heated to about 160° C. when the bulk of the water is driven off and some of the mineral matter settles out. The refined product—Trinidad épuré—contains about 38 per cent mineral matter. The bitumen of this lake is evidently still flowing into the depression as the level of the lake has only dropped very slightly although many millions of tons have been removed. It was first discovered by Sir Walter Raleigh in 1598.

A deposit of a somewhat similar character occurs at Bermudez in Venezuela which is almost opposite the Island of Trinidad. The bitumen contains from 10 to 40 per cent of water but this is not emulsified with the bitumen as is the case with the Trinidad asphalt.

The physical properties of asphalts derived from this source

vary somewhat due to evaporation of the volatile constituents and oxidation and other changes involved in weathering, thus, in the case of the Trinidad deposit the asphalt which overflows from the lake and is known as "land" asphalt contains less volatile matter and is harder than that obtained from the centre of the lake.

(c) *Impregnated Rocks and Soils.* The asphalts occurring in this way are not used to any extent by the varnish manufacturer. The most important deposit of this character is that occurring in Switzerland known as Val de Travers asphalt which is largely used in road making and paving.

2. RESIDUAL PITCHES FROM VARIOUS CHEMICAL PROCESSES

(a) *Petroleum Residue.* The distillation of mineral oil leaves a black pitch like residue the properties of which depend upon the nature of the parent oil, the method of distillation and the temperature to which it is carried. The product is often further modified by blowing air through it at a high temperature for several hours—from ten to fourteen hours at from 170° to 300° C. may be taken as general limits. The effect of blowing is to give the product a greater elasticity and a certain rubber like quality. Petroleum pitches are graded according to their hardness as indicated by their fusibility and the penetration test, i.e., the rate at which a standard loaded needle sinks into the mass at a definite temperature and under standard conditions.* The general limits are :

Fusibility ...	...	...	...	...	...	80°—225° C.
Penetration ...	...	...	...	...	...	0—150

These products contain only small quantities of mineral matter—less than 1 per cent—and except in the case of Mexican oils, practically no sulphur. They are completely soluble in carbon disulphide and in benzene. The harder varieties break with a conchoidal fracture.

(b) *Coal-tar Residues.* As in the case of the petroleum residues the composition and properties vary with the nature of the tar and the method and conditions of distillation. Thus with high temperatures and small charges the yield of pitch may be as high as 78 per cent whilst with continuous vertical retorts only 47 per cent is obtained.

* Reference A.S.T.M. 1916, p. 530.

(c) *Other Tar Residues.* Similar products are obtained as residues from the distillation of the tars obtained from coke ovens and blast furnaces, but these residues are of no great interest to the varnish maker.

(d) *Stearin Pitches.* On distilling fatty acids with superheated steam a black residue is left, the composition and properties of which, as in the case of petroleum and coal-tar, depend upon the nature of the parent substances and the method of treatment. Those placed on the market vary from soft sticky substances to hard brittle solids with a lustrous fracture. They contain from 5 to 10 per cent of free fatty acids and have usually a fairly high iodine value—from 60 to 120—thus indicating the presence of considerable amounts of unsaturated compounds.

Similar products of fatty nature are obtained in the course of refining cottonseed oil. The aqueous layer obtained after treating the raw oil with caustic soda contains the soaps of fatty acids, mucilage, etc. On treating this with mineral acid the fatty acids are liberated and rise to the surface bringing with them much of the impurity and colouring matter together with unchanged oil which had emulsified with the aqueous layer. The result is a black grease containing about 40 per cent cottonseed oil and 50 per cent fatty acids which is sold usually on the basis of 98 per cent soluble in carbon disulphide. On distilling with superheated steam, about 10 to 20 per cent of the black grease is left as a pitch like substance which varies from a hard brittle solid to a soft mass depending upon the circumstances of the distillation.

A similar type of product is obtained on the distillation of wool grease which is obtained in large quantities in wool scouring.

Bone-tar Pitch. Bones on dry distillation yield a tar known as dippe's oil which on distillation leaves a hard jet black pitch with a comparatively high melting point which is intermediate between the bitumens and the fatty acid pitches.

PRACTICAL TESTS

In using these materials the varnish maker is primarily concerned with their physical properties and compatibility with the other substances to be used with them.

In the case of an unknown substance, its origin may

invariably be detected by noting the odour on burning. Coal-tar pitches give an odour of phenol, bones of burning hair and stearin pitches a characteristic odour of burning fats.

Pitches of a fatty origin are further distinguished from the coal-tar and petroleum bitumens by the presence of fatty acids, the determination of which is occasionally desirable. In ordinary practice, a determination of the mineral matter, moisture and insoluble matter in a particular solvent is sufficient for the varnish maker.

USE IN THE VARNISH INDUSTRY

For the purpose of the varnish industry these materials may be summarised as follows :

1. *Natural Bitumens*, Gilsonite being a typical member of the group. These are hard brittle substances completely soluble in coal-tar hydrocarbons, turpentine and white spirit. In the last solvent, however, there is a tendency to gelatinise on keeping and, generally speaking, it is not advisable to use this solvent alone. The addition of a certain proportion of coal-tar naphtha is desirable. Natural bitumens are used in both stoving lacquers and bituminous paints, generally in conjunction with drying oils. Frequently natural resins are added, as of themselves bitumens give too brittle and light-sensitive a film.

2. *Petroleum Bitumens*. These are rather softer than Gilsonite though, generally speaking, they can be used almost equally well for the majority of purposes. They do not, however, give so dense a blackness in the finished product. In the case of the "blown" bitumens there is the advantage of an increased elasticity and stability.

3. *Stearin Pitch*. This is not used alone, but admixed with the other bitumens greatly increases the elasticity of the film and improves the durability of bituminous compositions by reducing the susceptibility to the action of light.

4. *Bone Pitch*, generally speaking, resembles stearin pitch but is much harder. It is not, however, used to a very great extent. In the best grades of japans it is used on account of the very intense black colour which it gives to the film.

MANUFACTURE OF BITUMINOUS VARNISHES AND LACQUERS

The use of bitumens in conjunction with oils presents some

difficulties. The most important points are temperature control during manufacture and the adjustment of driers.

Sufficient heating to ensure complete amalgamation of the ingredients is essential but, on the other hand, over-heating causes partial decomposition of the bitumen which results in reduced solubility and the formation of "free" carbon. On the other hand, insufficient cooking results in precipitation known as "seeding"; in extreme cases livering may occur.

With simple mixtures of linseed oil and Gilsonite and similar bitumens, the temperature may be kept down to 400° F. In any case it is advisable to heat the oil to the required temperature and then to add the bitumen slowly. When it is completely dissolved the temperature may be raised, sometimes as high as 500° F. without danger, depending on the nature of the bitumen and the other ingredients.

Driers. As regards driers, bitumens, particularly those derived from petroleum, have a distinct retarding action. With the hard varieties this is counteracted by increased hardness of the film as the proportion of bitumen increases.

This question has been dealt with very thoroughly by W. N. Bowran (*Jour. Oil and Colour Chem. Assoc.*, 1931, 14, 180) whose paper should be consulted. According to Bowran, as little as 5 per cent Gilsonite will increase the drying time of a linseed oil varnish from ten hours to fifty hours and it is not until about 50 per cent Gilsonite is reached that the hardening action counteracts the retardation of the drying.

An increased proportion of driers is therefore necessary and can be made without causing the defects which arise through excess of driers in the ordinary type of varnish. It appears that the bitumen actually absorbs the active constituent of the drier and thus reduces its effective concentration. Generally speaking, lead and cobalt are the most satisfactory but it must be borne in mind that an excess of driers, particularly lead, may cause precipitation in the varnish on storage.

Resins. Practically all the usual varnish resins can be used in conjunction with bitumens, the most generally used are the copals which are first incorporated with linseed oil in the usual way and the hot mixture added to the molten mixture of the bitumen and other fusible ingredients. As a typical example

of this type of product the following example may be given :

Portion A.

75 lbs. linseed oil

75 „ China wood oil

are mixed and heated to 400° F.

200 lbs. gilsonite

are added slowly and when dissolved, Portion B, which has been prepared simultaneously, is added.

Portion B.

56 lbs. Kauri gum

are run in the usual way and "oiled down" with

56 lbs. linseed oil

7 „ of litharge

are stirred in until completely dissolved. The temperature should be about 500° F. at the time the "run" is added to Portion A.

The mixed Portions A and B are heated to 560° F. and

4 lbs. manganese dioxide

slowly stirred in. When completely dissolved the temperature is allowed to fall to 500° F. and

16 lbs. litharge

added slowly. Care must be taken at this stage to avoid frothing over and it may be necessary to remove the pot from the fire.

When the addition is complete the pot is returned to the fire and the whole cooked until a cooled sample can be rolled to a pill between the fingers. The melt is then allowed to cool to about 350° F. and then carefully thinned with constant gentle stirring with

70 gallons white spirit

It will be noted that this japan contains about 4% lead on the non-volatile content, which is, of course, very much higher than would be permissible in an oil-varnish of a corresponding type.

The comparatively high temperature at which thinning is started is due to the fact that this japan corresponds to a "short oil" varnish in the proportion of resins and bitumen to oil and the first additions of solvent must therefore be made very slowly.

This black japan, if properly prepared, aged and filtered, should dry within four to six hours at normal temperatures, and in twelve hours permit of being lightly rubbed down with fine pumice and water on a felt pad. This treatment should not tear up the film which should present a smooth surface free from sweaty patches and a coat of varnish applied over it should not be affected in colour due to lifting of the undercoating japan.

This japan should mix with any type of oil varnish in

conjunction with which it can be used to form a lacquer for tinplate or iron or as a stain for wood work. Flat and semi-flat blacks, often called Berlin blacks, may also be prepared with a japan of this type by adding thereto suitable proportions of vegetable black ground in turpentine and/or white spirit, the degree of flatness being regulated by the proportion of thinner.

THE WEATHERING OF BITUMINOUS PAINTS AND VARNISHES

It has long been known that many varieties of bitumen both natural and residual are highly sensitive to the action of light, in fact, this property was utilised by Niepce (in 1824) in photographic processes. It appears that this property of sensitiveness to light is confined to certain constituents of the bitumen and that petroleum asphalts free from paraffins are the most sensitive. In addition to this photogenic action oxidation also occurs to some extent and the nett result is the appearance of fine cracks all over the surface and finally complete disintegration of the film.

These effects, however, vary greatly with the type of bitumen used and the treatment it receives during incorporation in the varnish. The literature of the subject abounds in contradictory statements as to the reliability of bituminous preparations as protective coatings on surfaces exposed to weather and sunlight.

From what has been said both with regard to the variety of bituminous substances and their sensitiveness to manipulation during the processes of varnish manufacture, it will be realised that sweeping generalisations are impossible and in our present state of knowledge it is practically impossible to differentiate between faults due to inherent deficiencies of the bitumens and those introduced through faulty methods of manufacture.

Bituminous paints and varnishes, however, are particularly valuable where protection against corrosion of metal due to moisture must be guarded against. Such preparations are largely used for the protection of water pipes, Dr. Angus' solution being the best known preparation.

The simplest types consist merely of asphaltum dissolved in turpentine or naphtha with perhaps some linseed oil added to increase elasticity.

It must be remembered that bitumens and pitches are cheap materials and large quantities are used quite legitimately in

very cheap products. It is not to be expected that products of this type will compare with the highest quality oil varnishes and paints in durability and many of the adverse criticisms of bituminous coatings are due to making this obviously absurd comparison. Bituminous varnishes and lacquers made of good materials and with due regard to the special properties of the bitumen used compare at least favourably with corresponding oil/resin preparations and have particularly high water resisting qualities.

Various types of pitches and bitumens are used for making "Brunswick black," "Berlin black," "black japan," "insulating black" and similar preparations for air drying and stoving varnish. These, if mixed with other classes of varnish form stains for wood. Whether they are for inside, outside, quick or slow drying purposes, such preparations may take the form of mixtures of the japan with ordinary gold size, cheap oak varnishes, japan gold size, u/c. varnishes, carriage or body varnishes and certain oil soluble types of dyestuff for yellow and red stains.

The ordinary kind of coal-tar and Stockholm tar is useless for the manufacture of Brunswick black or japans. They are used by themselves for wood preservatives and in some cases for coating ironwork.

CHAPTER XI

THE MANUFACTURE OF OIL VARNISHES

THE processes involved in the preparation of oil varnishes have been described to some extent incidentally to the description of the materials and plant utilised. It remains, therefore, to summarise the details and discuss the practical application of what has already been said with regard to the chemical and physical changes involved.

The various stages may be classified as follows :

1. Running the gum
2. Cooking the run gum with the oil
3. Cooling and thinning
4. Clarification

1. *Gum Running.* The selected resin is placed in the varnish pot and heated until sufficient decomposition has occurred to leave the residue in a condition such that it will form a stable mixture with the other ingredients.

This is a process requiring great care and experience. The resin is a poor conductor of heat and is reduced to a sticky viscous mass considerably below the temperature required to "run" it effectively. The gum runner must, therefore, keep the resin gently moving as otherwise some may stick to the bottom and sides of the pot and become charred, resulting in a dark coloured varnish and, if any considerable amount of resin is overheated it results in an unsatisfactory amalgamation with the liquid ingredients. As the temperature rises, vigorous frothing occurs and inflammable vapours are evolved in large quantities. Careful control of the fire and manipulation of the stirrer are therefore necessary. The attainment of the oil-soluble state is marked by an almost complete cessation of frothing and the molten resin flows off the stirring rod as a clear liquid.

The oil can then be added.

2. *Adding the Oil.* The oil must be hot and added slowly

with constant agitation. If the oil is too cold or the addition is too rapid the resin may be precipitated and it will be difficult, if not impossible, to re-dissolve it. The oil is, therefore, heated in another pot and at the right moment added to the molten resin.

3. *Cooking.* The oil having been added successfully, it is necessary to continue the heating. During this process the combination between the resin and the oil is completed and the mixture thickened. The driers can also be added at this stage and, generally speaking, it is advantageous to do so as during the cooking they are effectively combined with the oil and resin. The progress of these changes is observed by removing drops of the mixture from the pot and allowing them to cool on a glass or tin plate. Incomplete combination of the resin is invariably shown by the drop becoming cloudy on cooling. By observing the condition of the cooled drop the operator can decide when the operation is to be considered complete. In some cases a hard, solid drop is required while in others a certain degree of "stringiness" may be the objective.

In determining the end point of the process the varnish maker must allow for the fact that a large bulk of material will remain at a high temperature for some time after removal from the fire, and, therefore, thickening will continue.

4. *Adding the Thinners.* This operation requires attention to several points. The thinners being volatile must obviously be added with due precaution against fire and the thinning shop must be effectively screened from the gum running plant (see page 8). If the temperature of the varnish is too high the loss of volatile thinner will be excessive, while if it be too low precipitation may occur. The temperature selected must, therefore, be a compromise between these two. As a rule a temperature of about 300° F. is satisfactory, as this is just above the initial boiling point of turpentine or the grade of white spirit used in varnish making.

It is necessary that the addition be made slowly with constant agitation as, particularly with white spirit, too rapid cooling or a local excess of thinner may cause precipitation. If desired, driers can be added with the thinners.

The finished varnish is then sent to the stores. In the case of varnishes containing resins which are likely to enclose any appreciable amount of insoluble matter such as vegetable

debris, it is advisable to subject the varnish to a rough filtration by passage through a fairly fine metal gauze (about 60 mesh) immediately it is finished, as prolonged contact with such matter discolours the varnish. On the other hand, it is not advisable to remove entirely *all* the fine suspended matter as these minute particles form nuclei round which the precipitates always formed during storage accumulate. This, however, will be discussed in the chapter on varnish filtration (see page 101 *et seq.*).

As examples of procedure in oil varnish-making, the following cases may be given. In practice, the size of the batch of resin which can be handled in the pot depends upon the nature of the resin and the skill of the operator. In the case of the more easily manipulated resins such as Kauri and some grades of Manila, a practised gum-runner will work with as much as 1 cwt. of resin. At the other extreme, with very hard resins such as best Sierra Leone or very frothy resins such as most South American copals, the limit is about 60 lbs.

One frequently meets varnish makers who boast of being able to run extremely large batches of resin, but in practice this does not necessarily make for economy. The increased difficulty of properly manipulating the large mass of resin leads to greater irregularities in the result, while the greater time required to heat the mass or, if necessary, to cool it makes it difficult to control the temperature sufficiently accurately, besides increasing the danger of fire. It is usually better to run several batches of manageable size and then mix them in a larger pot for "oiling down." Small variations in each batch then average out and a uniform product is ensured.

SELECTION OF RESIN

Apart from the physical and chemical properties of the resin already discussed, the varnish maker has to take into consideration the cost of the varnish. So far as the resin is concerned the main factors are :

1. The loss which will be incurred in the gum running process.
2. The volume of the residual run gum.
3. The amount of oil and thinners which will be required to give the desired properties in the finished varnish.

As regards losses in gum-running the following is an approxi-

mate estimate for some of the principal resins, but of course much depends upon the skill of the operator, the conditions under which the operation is performed, and the grade of resin used.

Sierra Leone copal	...	...	...	...	12—15	per cent
New Zealand kauri	...	...	...	...	12—15	" "
Congo copal	...	...	...	...	25—35	" "
Benguella copal...	...	...	...	...	20—25	" "
Pontianak (best)	...	...	...	...	20—25	" "
Manila copal	...	...	...	...	25—35	" "
Angola copal	...	...	...	...	20—25	" "
Zanzibar animi	...	...	...	...	15—20	" "

When properly run in such a way as to give losses of this order, the residual fluid resin bulks about 12 lbs. to the gallon and 100 lbs. of resin yield the following amounts of fluid run gum :

Sierra Leone copal	...	...	...	...	7	gallons
Angola copal	...	...	...	...	6	"
Congo copal	...	...	...	...	4½—5½	"
Kauri	...	...	...	...	6½	"
Pontianak	...	...	...	...	5½	"
Hard Manila	...	...	...	...	5½	"
Zanzibar animi	...	...	...	...	6½	"

As an illustration of the bearing of these factors on the cost of a varnish, a comparison may be made between Sierra Leone and Congo copal.

1. When "run," 100 lbs. of Congo will yield only about 5 gallons of run gum, whereas Sierra Leone will yield nearly 7 gallons. Weight for weight one therefore obtains more resin in the finished varnish with Sierra Leone and also higher gloss. Conversely, one can use more oil (which is cheaper than resin) to give the same ratio of oil to resin.

2. Under the same conditions, Congo copal darkens to a greater extent than Sierra Leone in the running process.

3. The resulting run gum has a lower acidity in the case of Sierra Leone copal.

4. Except in the case of the highest grades of Congo, the insoluble matter is usually higher than in Sierra Leone copal which in fact gives a lower percentage of insoluble matter than any other resin.

To summarise these results a balance sheet may be made out for two similar varnishes, the one with Sierra Leone and the other with Congo copal.

1. <i>Congo copal.</i>			<i>Cost.</i>
100 lbs. copal yield	5 gallons run resin		150/-
Linseed oil	25 "		62/6
Turps.	20 "		50/-
Driers	*		*
Finished varnish	50 "		262/6
<i>Per gallon 5/3</i>			
2. <i>Sierra Leone copal.</i>			<i>Cost.</i>
100 lbs. copal yield	7 gallons run resin		300/-
Linseed oil	25 "		62/6
Turps.	25 "		62/6
Driers	*		*
Finished varnish	57 "		425/-
<i>Per gallon 7/6</i>			

It will be observed that although the price of the Sierra Leone has been taken as twice that of the Congo copal the prices of the finished products are in a much lower ratio.

CLASSIFICATION OF VARNISHES.

It is usual to base the formulæ of varnishes on 100 lbs. weight of resin and to divide them into three classes according to the proportion of oil. Taking the oil as 9 lbs. to the gallon the scheme can be arranged as follows :

	LONG OIL.	MEDIUM OIL.	SHORT OIL.
Resin lbs. ...	1, 2, 3, 4	5, 6, 7, 8	9, 10, 11, 12, 13, 14
Oil " ...	9, 9, 9, 9,	9, 9, 9, 9	9, 9, 9, 9, 9, 9
% resin ...	10, 18, 25, 31	35, 40, 44, 47	50, 52, 55, 57, 59, 61

As examples of varnishes made with natural resins the following may be taken :

- Long oil varnish.*

56 lbs. Congo copal ...	...	...	} 36 gallons finished varnish
12 gallons linseed oil	...	...	
6 " China wood oil	...	...	
$\frac{1}{2}$ lb. cobalt linoleate	...	...	
4 lbs. litharge	...	...	
8 gallons turps.	...	...	
8 " white spirit	...	...	
- Short oil varnish.*

56 lbs. Sierra Leone copal ...	...	...	} 20 gallons finished varnish
6 gallons linseed oil	...	...	
4 lbs. litharge	...	...	
$\frac{1}{2}$ lb. cobalt linoleate	...	...	
5 gallons turps.	...	...	
5 " white spirit	...	...	

3. *Medium oil varnish.*

56 lbs. Congo copal	} 26 gallons finished varnish
5 gallons linseed oil	
4 „ China wood oil	
3 lbs. litharge	
$\frac{1}{2}$ lb. cobalt linoleate	
12 gallons white spirit	

VARNISH MAKING PLANT

The essential equipment of the varnish maker's plant consists of :

1. *Running Pots*, in which the resin is melted.
2. *Boiling Pots*, used for heating the oil and the finished product.
3. *The Pot Carriage*, by means of which the pot can be removed from the fire while at high temperatures.
4. *Thermometers*.
5. *Stirrers*.
6. *Fume Condensers*.

1. *The Gum Running Pot.* Various metals have been used from time to time for making gum running pots. Many years ago they were invariably made of copper as this metal has the highest conductivity for heat and wears well. Welded steel can also be used. More recently, aluminium and various aluminium alloys have been introduced. The advantage of these is that they do not colour the varnish by reason of the formation of coloured salts formed by the action of the acidic constituents of the resins on the pot. Also aluminium is much lighter than either iron or copper. Generally speaking, however, aluminium and aluminium alloys are not so durable as copper or iron and in modern practice a compromise is usually made. The bottom of the pot which has to withstand a very high temperature and frequently local over-heating, due to the poor conductivity of the resin, is made of copper while the sides are made of aluminium alloys. It has been found that most of the reaction between resin and the pot takes place at the surface of the liquid, and consequently by this means one obtains the advantages of both metals. There is also a further advantage in that the bottom can be replaced should it become worn out, as invariably happens, long before the upper portion of the pot.

As it is necessary for the resin to be exposed to the full heat of the fire, the joint between the bottom of the pot and the walls is usually made with a flange so that it can rest in the furnace as shown in the illustration (Fig. 4).

2. *Boiling Pots.* These can be made of similar materials to the gum-running pots, but frequently enamelled iron is used. If aluminium is used it is desirable to have a copper bottom, though this is not so essential as in the case of the gum-running pot.

3. *The Pot Carriage.* The construction of this is easily seen

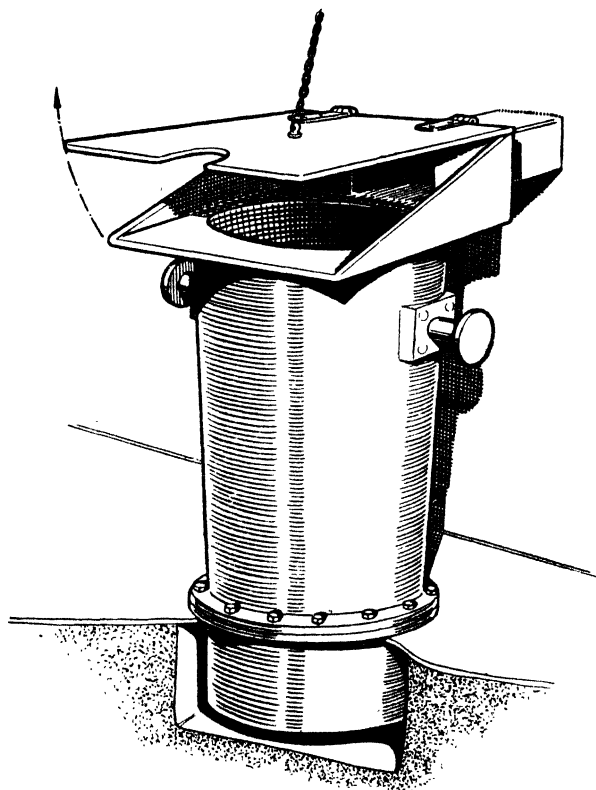


FIG. 4.

from the illustration (Fig. 4). It should be strongly made and kept in good order so that there is no danger of it jamming or breaking down at a critical moment. In the event of a pot becoming overheated or actually catching fire, it is necessary to run it out of the furnace-room into the yard as quickly as possible and consequently the pot carriage should always be ready for use at a moment's notice.

4. *Thermometers.* These should be very strongly constructed and preferably enclosed in steel. The dial pattern is best.

5. *Stirrers.* These may be made of either iron or, better still, aluminium, which, apart from the fact that it does not discolour the varnish, has the advantage of being light in weight.

6. *Fume Condensation Plant.* The condensation of fumes in a varnish factory is an extremely important matter. Quite apart from the danger of fire and the convenience of workers in the factory, the creation of noxious fumes is liable to incur a visit from the local authorities with unpleasant consequences to the varnish maker. Each gum-running pot should be provided with a hood. Various types have been designed, but the one shown in the sketch is quite satisfactory. They can be made of aluminium, but galvanised iron is quite satisfactory if of the best quality. The hood must be easily detachable so that in the event of it being necessary to remove the pot from the fire, no time will be lost in taking off the hood. It is, therefore, made so that it can be pushed up out of the way by means of counterpoised pulleys or can be removed readily with the pot. The flues from each varnish pot lead to a main flue in which all the fumes of the varnish plant are treated. In the old type of plant, condensation was effected simply by making the flue of sufficient length and finally leading it into a chimney in which a small fire was kept burning. It was thus hoped to burn up all the uncondensed fumes. In practice, however, this was not entirely effective and there was also the danger of a fire starting in the flue. In the most modern practice a series of water sprays is arranged in the flue so as to isolate each varnish pot and effectively condense the great proportion of the fumes. The fume-duct is led into a separating tank containing water where the condensed matter rises to the surface and can be collected. The water from this tank is drawn off by means of the pump and again fed to the sprays. In this way the water consumption is kept down to a minimum. Such fumes as escape this process pass to the main chimney of the factory.

SPECIAL GUM RUNNING PLANTS

Recently special plant has been constructed in which gum-

running is reduced to a purely mechanical process. The chief difficulty in designing a plant capable of doing this is that of heating the resin in such a way that excessive frothing does not occur and at the same time agitating it in such a way as to avoid local overheating. It has been found possible to surmount these difficulties with some success by the use of a totally enclosed plant to which carbon dioxide is supplied, thus eliminating the danger of fire and also oxidation of the resin.

The pot is filled to about one-quarter its capacity with the resin and then closed, carbon dioxide being pumped in through the cock. Heating then takes place until the resin becomes sufficiently molten to be stirred, when the stirring gear is started up. The formation of foam is reduced to a minimum by the action of the stirrer and by the carbon dioxide. The fumes pass off through a pipe and into a separator, which is supplied with a water spray, where they are condensed. Samples can be taken during the running, and when the copal is sufficiently run the hot oil and driers can be fed in through an inlet in the cover. When the varnish has been thoroughly cooked it is forced out of the pot by means of pressure applied by the carbon dioxide.

CHAPTER XII

SPIRIT VARNISHES AND STAINS

THE MANUFACTURE OF SPIRIT VARNISHES

THE preparation of a spirit varnish is essentially a process of solution followed in most cases by clarification. At the same time it is necessary to bear in mind the nature of the relationship between the resin and the "solvent" which has been discussed previously (see pages 2 and 39).

Some form of agitation is necessary to ensure sufficiently rapid dispersion of the solid ingredients and in some cases it is necessary to store the varnish for a time to ensure the precipitation of all the impurities.

As regards solution, the most general means is some form of churn. The simplest form is a wooden barrel mounted horizontally on trunnions. Usually the mounting is eccentric so that there is an oscillating as well as a rotating motion. Occasionally the reverse process is adopted, the container being stationary and agitation effected by means of a stirring device. Generally speaking, however, this is not so satisfactory or economical as the totally enclosed churn which entirely eliminates loss by evaporation and the entrance of dust and extraneous materials.

As regards clarification, shellac varnish is in a class by itself as the wax, which does not completely dissolve in methylated spirit, is an essential ingredient of the varnish, consequently, shellac varnish of the type generally used in the varnish trade is of necessity turbid and cannot be clarified by filtration. In certain special cases, however, the wax is not required and in such cases it is usual to use a wax-free shellac.

The plant for filtering spirit varnishes is dealt with in Chapter XIII.

FORMULÆ FOR SPIRIT VARNISHES

In drawing up a formula for spirit varnishes allowance must be made for the undissolved matter, moisture and loss by evaporation. This is best done by making a laboratory trial.

A known weight of resin is dissolved in the selected solvent mixture and the volume and weight per gallon of the solution noted. The solid content is then determined by evaporating a known weight of the varnish and weighing the residue.

In most cases it is advisable to prepare stock varnishes of known composition each containing a single resin or a mixture of resins of general utility. It is then possible to make up most of the varnishes generally required by blending the stock varnishes.

The following typical varnishes are discussed in some detail as illustrating the general principles involved :

SHELLAC POLISHES AND VARNISHES

The solvent in this case is methylated spirit and the solid content varies from $2\frac{1}{2}$ to $3\frac{1}{2}$ lbs. per gallon. In the best qualities pure shellac—usually the standard commercial grade, TN, is used. The resin is dissolved in the cold solvent and as already explained is not filtered. In certain cases where it is desired to increase the elasticity of the varnish about 2 per cent of plasticiser is added. Castor oil is the most convenient and cheapest plasticiser and gives quite good results, though it is claimed that some of the newer synthetic plasticisers such as tri-cresyl phosphate are even better.

In cheaper grades of varnish a certain amount of other alcohol-soluble resin is added. Rosin is the cheapest of these, but Manila copal which does not so adversely affect the film is often used. For darker coloured varnishes button lac or garnet lac can be used, while for white transparent varnishes bleached lac must be used. In this latter case it is important to remember that commercial bleached lac contains varying proportions of water, often as much as 25 per cent. The "bone dry" grades recently introduced contain between 3 and 5 per cent. Allowance for this moisture must be made in calculating the weight to be used to give the desired resin content to the finished product.

As typical varnishes of this group the following may be quoted :

BROWN HARD SPIRIT VARNISH.

4 lbs.	Manila copal
2 „	Garnet lac
2 „	rosin
1 gallon	methylated spirit

VARNISH MAKING

KNOTTING OR FRENCH POLISH.

3½ lbs. TN shellac
1 gallon methylated spirit

KNOTTING.

3 lbs. TN shellac
1¼ „ Manila copal
1 gallon methylated spirit

WHITE POLISH.

4 lbs. bleached shellac (dry weight)
1 gallon methylated spirit

SANDARAC VARNISHES.

White hard spirit varnishes.

1.

5 lbs. sandarac
3 „ rosin
1 gallon methylated spirit
2.

3 lbs. sandarac
½ „ elemi
1 gallon methylated spirit

The elemi improves the elasticity and it is advisable to dissolve it in the methylated spirit before the sandarac.

WOOD VARNISH (FOR HIGH CLASS CABINET WORK).

1 lb. sandarac
½ „ mastic
2 „ rosin (W.W. grade)
3 „ gum benzoin
1 gallon methylated spirit

The function of the rosin is to improve the solubility of the mastic and the sandarac and thus give more stable solution while the benzoin improves the elasticity and gives a smooth and brilliant film.

MANILA COPAL VARNISHES

The soft, alcohol-soluble grades of Manila copal are very largely used in spirit varnishes. A certain amount of the resin, however, frequently will not dissolve or may be precipitated after the varnish has stood some time. The addition of small amounts of rosin tends to prevent this to a great extent. Manila copal is also used in conjunction with shellac, examples of this have already been given.

1. *Paper varnish.*
2 lbs. Manila copal
1 lb. rosin
1 gallon methylated spirit

2. *Varnish for wood.*
8 lbs. Manila copal
1½ „ mastic
1 lb. Venice turpentine
1 gallon methylated spirit

The Venice turpentine acts as a plasticiser. A small amount of camphor (about an ounce) can be added to improve the stability of the solution, and the transparency of the film.

DAMAR VARNISH

Damar varnishes may be made using either turpentine, white spirit or coal-tar naphtha as a solvent.

The solutions in coal tar hydrocarbons are the most stable, but those in white spirit are apt to precipitate. Batavian damars are the most reliable in this respect, but Singapore damars are liable to give trouble. As white spirits of different origin contain varying amounts of aromatic hydrocarbon their solvent power varies considerably. It is therefore necessary to be particularly careful that both the damar and the white spirit used are consistently of the quality found to be satisfactory. Turpentine solutions are invariably opalescent, but are more stable than those in white spirit.

Varnishes made with damar are pale and give a fine glossy finish, but the films are soft and lacking in durability and they can therefore only be used for interior work. As the film tends to become slightly sticky with the warmth of the hand, damar varnish should not be used on objects which are much handled. Formerly damar was largely used in paper varnishes, but has been largely replaced for this purpose by cellulose varnishes.

CRYSTAL VARNISH.

8 lbs. damar
1 gallon turpentine

VARNISH MAKING

PAPER VARNISHES.

1.

17 lbs.	damar
2 „	rosin
$\frac{1}{2}$ gallon	turpentine
1 „	white spirit
2.

18 lbs.	damar
$\frac{3}{4}$ gallon	white spirit
$\frac{1}{4}$ „	xylol (solvent naphtha)

MASTIC VARNISH.

Common varnish.

3 lbs.	mastic
2 „	rosin (W.W.)
3 „	damar
1 gallon	turpentine

PHOTOGRAPHIC VARNISH.

Damar	...	...	...	...	8 lbs.
Benzene	...	...	...	...	1 gal.
Methylated Spirit	...	...	...	...	1 pint.

Alcohol must be used with caution in damar varnishes as it is not a solvent for damar, and may therefore cause precipitation if used in excess.

MATT VARNISH.

Damar	...	...	...	...	20 parts
Turpentine	...	...	...	...	30 parts
Beeswax	...	...	...	...	5 parts

Other waxes may be used, and in some cases as much as 10% wax may be added.

SPIRIT STAINS

The production of these has been rendered very simple by the introduction of synthetic dyes, many of which are soluble in the solvents used in the preparation of spirit varnishes. The selected dye is dissolved in the solvent with the resins or added subsequently to the stock varnish as required. From 2 to 3 ozs. of good quality dye per gallon of varnish is sufficient for most purposes. It should be noted that the purchase of cheap dyes of doubtful origin is invariably false economy. These are frequently loaded with dextrin, starch or similar material which, of course, is quite useless, if not actually

harmful, in the finished product. A series of good dyes should be selected and adhered to consistently.

Stains made in this way are transparent and it is important that the degree of fastness to light of the dye used should be known—another reason for adherence to dyes of standard quality.

PIGMENTED SPIRIT STAIN

Pigmented stains are sometimes used. Generally these are not so transparent as dye stains, but the fastness to light and durability may be greater. The selected pigment is simply ground in the spirit varnish ; if, however, a plasticiser is used the pigment is best ground in this, using an ordinary paint mill for the purpose. If a ball mill is available the final grinding is most conveniently done in this, the pigment, preferably ground in the plasticiser, and the varnish being all treated together therein.

It is necessary to select the pigments with care as many of the resins used are acidic bodies and consequently may react with the pigment. A more frequently occurring trouble is coagulation of the pigment. The fundamental causes of this trouble are as yet incompletely understood and it is necessary to test out carefully any new pigment which it is proposed to use.

WATER STAIN

The simplest form of water stain consists merely of a dextrin or glue (size) solution coloured with a water soluble dye. As glue, dextrin and similar products provide nutriment for moulds and bacteria it is essential a disinfectant should be added. Carbolic acid is highly effective but may be objectionable. For certain purposes boric acid is quite effective and being odourless and less chemically active is frequently preferred. β -naphthol, cresol and salicylic acid are also useful preservatives.

SHELLAC WATER VARNISHES

Shellac is soluble in alkaline solutions :—Sodium carbonate, borax (sodium borate) and ammonia are the chief. On evaporation such solutions leave a film which is fairly resistant to water. The solution of the shellac is a somewhat delicate operation,

as unless performed correctly a hard coagulated mass of shellac is formed which is difficult to dissolve and, sticking to the bottom of the vessel, is liable to be charred.

The borax is dissolved in the requisite amount of water, usually enough to give a 10 per cent solution, and the powdered lac added slowly with constant stirring to the solution which is kept at about 60° C. (*not boiling*). The solution so obtained can be diluted if desired. Pure crystallised borax will dissolve about six times its weight of shellac.

Solutions in ammonia are not so much used in the preparation of water stains, but a small amount of ammonia is sometimes added to the borax solution to improve the solubility. In preparing ammoniacal solutions of shellac the shellac should be steeped in the ammonia (Sp. G. 0.91) overnight or until it forms a gelatinous mass.

CHAPTER XIII

CLARIFICATION OF VARNISHES

IT has already been explained that a varnish is not strictly speaking a solution, but is essentially colloidal in character. This distinction is particularly important in considering the process of clarification. In addition to the removal of insoluble suspended impurities derived from the raw material there is also to be considered the gelatinous deposits formed by the slow interaction of the constituents over a considerable period after the varnish has been made. Apart from their slimy nature, which renders filtration through paper or cloth difficult, the fact that these deposits are of very nearly the same specific gravity as the varnish makes their separation by sedimentation, even when accelerated by centrifugal force, difficult. The relatively high viscosity of most varnishes also retards both filtration and sedimentation.

It is evident from the above that time being an essential factor in the formation of the deposits storage cannot be entirely eliminated, but nevertheless the length of storage can be substantially reduced and the clarity of the varnish much improved by the judicious application of filtration processes. Filtration has the further advantage that the impurities are removed in a compact form with a minimum of loss due to entrained varnish. It is also desirable to remove the grosser impurities such as undissolved or charred gum and vegetable debris as soon as possible, as these are liable to discolour the varnish if left in contact with it. A preliminary filtration of the varnish soon after manufacture by passage through a centrifugal machine is therefore desirable. It is not necessary or even advisable at this stage to remove the finer impurities for these act as a nuclei round which the precipitates formed during storage can accumulate and thus sedimentation is hastened. After the varnish has been stored for a certain time, depending upon its nature, the final clarification can be

made. This can be effected by either the centrifugal machine or the filter press—probably the best method is to combine the two, using the centrifugal machine to remove the bulk of the impurities and the filter press for a final clarification—in this way the deposits on the filter cloth are reduced to a minimum, with the result that the press can run for a longer time and the output is maintained at a higher figure due to the reduced thickness of the deposit.

The filter press, however, suffers from the disadvantage that in any case a very considerable volume of varnish is required to fill the press, and that before it can be used for another varnish the whole press must be cleared and new cloths and papers fitted. Both the filter press and centrifugal machine have, therefore, a definite function in the varnish factory and a judicious use of both is of great advantage both as regards the efficiency of the factory and the quality of its products. These remarks apply also to spirit varnish, though in most cases not to the same extent. The question of the loss of volatile solvent, however, is more important. In the case of the filter press, the exposed edges of the cloths and paper present a very large area from which evaporation can occur, and consequently a totally enclosed form must be used. This also applies though not quite to the same extent in the case of centrifugal machines.

The plant available to the varnish maker may, therefore, be discussed under three headings :

1. Filtration through membranes, e.g., filter press
2. Clarification by centrifugal force
3. Special machines combining both processes

1. MEMBRANES

Most makers still maintain that filtration through a membrane without any pressure other than that of a small head of varnish is the most satisfactory. Certain types of shellac varnish are still filtered through by conical cloth bags. In any case it is certainly desirable to keep the pressure as low as possible even when using the filter press, as beyond a certain point additional pressure simply forces the gelatinous matter into the pores of the paper and merely chokes them the more effectively. For this reason the use of a filter aid is certainly advisable and, even when the centrifugal machine is used, the action of the filter aid is beneficial as forming a foundation

for the impurities and thus giving a more effective separation and a more easily handled cake of residue.

Filter Aids. These consist of specially prepared substances, such as china clay, fuller's earth, kieselguhr and diatomaceous earth which have a high absorptive power for colouring matters and impurities. When used in filter presses about 1 lb. of filter aid per square foot of filtering surface is required and this amount is mixed with part of the varnish and passed through the press at a low pressure, thus forming a cake over the whole surface before the main batch of varnish is treated. In the case of centrifugal machines about 1 per cent of filter aid is mixed with the varnish before it passes through the machine.

Filter Presses. The simple flush plate and distance frame type of press can be used as it is not desired to recover or wash the residue.

One of the holes at the bottom of each plate is used as an inlet and the other as an outlet for the varnish left in the press at the end of the operation. Various types of filter plates have been suggested the main differences being in the arrangement of the supporting studs; usually the ordinary type with rectangular studs is used, but it is claimed that diamond shaped studs arranged so as to guide the varnish to the outlet hole at the bottom corners of the plate present some advantage.

As regards the filtering medium it is desirable to cover the cloth with paper as this protects the surface of the cloth and helps to prevent choking. A crêpe paper is better than a plain paper in that it affords a larger filtering area. Usually the paper for varnish filtration weighs about 35 to 40 lbs. per ream (2 ft. by 2 ft.).

As regards pressure, if time permits an ordinary gravity feed with about 10 to 15 ft. head of varnish is quite satisfactory, and this has the advantage that the apparatus requires practically no attention. Wear and tear is reduced to a minimum and a comparatively lightly constructed press can be used.

Where mechanical pressure is applied, from 20 to 40 lbs. per square inch covers practically the whole range of pressure required, and for a press with about 250 square feet filtering area a pump delivering from 5 to 7 gallons a minute will be sufficient.

2. CENTRIFUGAL MACHINES

The centrifugal machines used in varnish manufacture are of three types :

1. High speed "super centrifugal"
2. Medium speed
3. Combined centrifugal and filtration machines

High Speed Type. The Sharples machine is typical of these ; it consists essentially of a long, narrow steel cylinder about 30 in. long and $4\frac{1}{2}$ in. diameter suspended in a ball race. The speed of rotation varies from 5,000 to 15,000 r.p.m., which is well above the critical speed of the system and consequently the bowl takes up a stable position whilst owing to the comparatively small diameter the disruptive forces are kept within safe limits. When used at the highest speed the force acting on the contents is about 17,000 times gravity and consequently separation is very rapid.

The varnish enters at the bottom of the bowl and emerges at the top, the solid matter being thrown out against the sides. The degree of separation can obviously be regulated either by cutting down the speed of the machine or increasing the rate of flow of the varnish through the bowl. In the case of oil varnishes, when working at full speed the delivery is at the rate of 50 to 150 gallons an hour, and 40 to 90 gallons for the thicker spirit varnishes. Shellac varnishes which are comparatively thin can be dealt with at from 90 to 200 gallons an hour. The bowl is easily removed and cleaned by passing a special ramrod down it. The capacity of the bowl is about 10 lbs. and the sediment is thrown out in a very compact dry form. The small capacity of the bowl also reduces the loss of varnish to a minimum. The length of time the machine will run without cleaning depends, of course, on the viscosity of the varnish and it is necessary to carefully study the condition of the outflow when dealing with a new varnish as a small amount of imperfectly clarified varnish coming over at the end of the run will contaminate the whole batch—for this reason it is desirable to put a small intermediate receiver between the machine and the main storage tank. With ordinary varnish such a machine will generally run at full capacity for at least five hours without cleaning so that if the bowl is cleaned at midday and at the end of the day, one is well within safe limits.

Medium Speed Machines. These usually run at from 2,000 to 5,000 r.p.m. The bowl is considerably larger and in the De Laval machine which is typical, the clarification is further assisted by a series of cones up which the varnish passes. The solid matter is thus forced between the surfaces of these cones and forced downwards by centrifugal action and finally flung against the sides of the bowl. The capacity of these machines is of the same order as that of the Sharples, but on the other hand the solids are generally not quite so dry and the bowl is larger and heavier, thus making cleaning rather more difficult.

3. COMBINED CENTRIFUGAL AND FILTERING MACHINES

The action of the centrifugal machine is strictly limited to cases where there is a difference of specific gravity between the solids and the liquids and where this difference is very small the rate of separation is correspondingly reduced. In the case of varnishes these differences are always comparatively small and some of the gelatinous particles differ only very slightly, if at all, in specific gravity from the varnish. Consequently the use of a filtering membrane is necessary in many cases. As already suggested the final passage of the varnish through a filter press is often advisable. Machines have been constructed in which the centrifugal force in addition to throwing out the solid matter is also used to force the varnish through a membrane.

STORAGE OF VARNISH

Whatever mechanical process may be used to accelerate the clarification of the varnish it is essential that the varnish should be stored for some time.

The design of the varnish store is, therefore, a matter of some considerable importance.

The capacity of the store house should be ample, allowance being made for storing certain varnishes for as long as two years. The size of the individual tank is, of course, a matter for the decision of the works' manager, but though large tanks are on the whole the most economical it is obviously undesirable to have them so large that they cannot readily be emptied for cleaning or the total contents used up within a reasonable time, or on the other hand are never utilised to full capacity. For

most purposes 1,000 gallons is a convenient size and for varnishes stored in large quantities 2,000 gallons.

The varnish store should be a substantial, weather proof structure and provided with heating arrangements so that an even temperature of about 70° F. can be maintained. If the varnish is allowed to become too cold an undue amount of the driers (particularly lead soaps) may separate, whilst owing to the greater viscosity of the varnish at low temperature the rate of sedimentation will be much reduced. On the other hand at high temperature material remains in solution which ought to be separated, with the result that the varnish becomes cloudy when exposed to ordinary atmospheric conditions. This question of temperatures has to be considered in determining the time it is estimated the varnish must be stored. Storage during the hot summer months obviously will not precipitate all the matter which will be precipitated during the winter. Careful testing of all varnishes for clarity at the time of dispatch is always essential (see Chapter XIV).

CHAPTER XIV

TESTING OF VARNISHES

THE testing of varnishes may be undertaken either with the object of matching the sample or determining its properties and whether or not it fulfils the demands of a certain specification.

In either case both physical and chemical tests are necessary. Although chemical tests in the hands of an experienced operator yield valuable information, their value is limited by the fact that the properties of a varnish, as will be evident from the preceding pages, depend largely upon the treatment the ingredients have received in the manufacturing process. It is necessary, therefore, that all chemical tests should be interpreted in the light of information obtained by parallel tests made on varnishes, the composition and method of manufacture of which are known in detail.

PHYSICAL TESTS

Colour and Appearance. The varnish should be carefully examined in a clear glass phial and its colour and freedom from foots noted. It is desirable that the sample should be allowed to stand for some time and the formation of foots noted. The behaviour on chilling the sample is also important, as varnish clarified at relatively high temperature may deposit foots on cooling to winter temperatures.

Odour. The odour will often give some indication of the thinners used, though comparatively small proportions of such substances as pine oil will effectively mask the odour of the main ingredient.

Viscosity. For many purposes a "bubble" test is sufficient. The varnish is placed in a standard tube and the cork adjusted so as to give a bubble of the same size as that in an *exactly*

similar tube containing the standard varnish. The tubes are placed in a bath at a definite temperature and after a reasonable time (e.g., about fifteen minutes at 20° C. is usually satisfactory), the two tubes are removed and rapidly inverted. The rate at which the bubble of air rises in each gives a comparative estimate of the viscosity. If a series of standard tubes containing varnishes or oils of known viscosity be prepared this method will give a sufficiently accurate estimate of the viscosity in absolute units for most commercial purposes.

The accurate determination of viscosity in absolute units should be made according to the precise directions laid down in the B.E.S.A. Specification No. 188. Although apparently complicated the procedure is not difficult or tedious when once the apparatus has been set up and standardised and its use in the works laboratory should be encouraged.

Drying Properties. This, of course, is the test of most commercial importance and involves observation of the following points. (1) The times required for the film to become tacky, dry to touch and hard must be noted and (2) the quality of the film as regards elasticity and so forth must be judged.

These observations are obviously matters of personal judgment, though various attempts have been made to devise standard mechanical tests. Films should be prepared on glass and on metal and all tests should be in duplicate.

The film on glass can be used for determining the drying time and hardness of the film and observation of its smoothness and freedom from blemishes, whilst the film on metal can be used for testing the elasticity. The progress of drying is noted by testing the film with the finger and comparing the results with those obtained in a parallel test on the standard varnish.

The point at which the film can be described as surface dry can be determined by placing sand on the film and after a definite time (say thirty seconds) endeavouring to brush it off with a camel hair brush. The time after which this can be done may be taken as that required to attain surface hardness. A more severe test is made by placing tissue paper on the film and putting a known weight on it for a given time. The time after which the paper ceases to adhere to the film is noted.

To the experienced person much information can be obtained by scratching the film with the finger nail and with a penknife.

Hardness Testers. Various machines have been devised from time to time with the object of giving a more or less quantitative measure of the hardness. Most of these machines depend upon the action of a weighted needle with a standard point. The varnish film is drawn under the needle and the minimum pressure required to produce a scratch on the film noted.

Though such instruments are very useful, and doubtless will be more widely used in the future, no machine can entirely replace the personal experience obtained by testing the film with the finger, and the student is recommended to obtain as much experience as possible, particularly with varnishes of known composition, and to compare his conclusions as to the quality of the varnish with the results obtained with it in industrial application.

Elasticity. The behaviour of the film on metal when the metal is bent gives an indication of the brittleness or otherwise of the film. In making comparative tests it is important that the conditions should be exactly the same in each test. The thickness of metal, the rate and extent of bending must be standardised. Tin or aluminium of 28 S.W.G. is usually prescribed in specifications and bending is effected by placing the sheet over a $\frac{3}{8}$ " cylindrical rod and bending sharply through 180°, a medium or elastic varnish should show no cracks under this test. It should be noted though, that this test is influenced very largely by temperature, the thickness of the film and its condition at the time of testing, consequently every precaution must be taken to ensure that comparisons are made under strictly parallel conditions. It is not possible, for example, to judge the result of a test made upon one day by mere reference to one made even a day or two previously unless, of course, a room kept at constant temperature and humidity is available for all such tests.

Accelerated Test. Even with air drying varnishes valuable information can be obtained by drying the film at a higher temperature. In most cases two hours at 100° C. is sufficient to dry the film and the bending test should be made after giving the panel half an hour to attain room temperature. Short oil varnishes dried in this way invariably crack under the bending test and if much rosin is present the film is frequently mottled or streaked. A varnish which presents this

appearance or fails under the bending test is evidently of low durability and unsuitable for outside work.

Water Test. The behaviour of the varnish film on glass when immersed in water is important. Rapid whitening of the film indicates the presence of much rosin or of excessive drier. A good outside varnish will whiten to only a slight extent and the film be in quite satisfactory condition when removed from the water after twelve hours and dried. The whiteness should disappear in a short time. The test can be further extended by alternate immersion and drying.

Brushing Test. It is essential that the behaviour of the varnish when applied by the method for which it is specially designed should be tested. In the case of oil varnishes which are to be applied by the brush, a practical test must be made and particular attention paid to the ease or otherwise with which the varnish can be handled and the way in which the brush marks and air bubbles disappear. The brushing test will also reveal the presence of suspended impurities of a gelatinous nature which cannot be seen by mere visual inspection of the varnish. The varnish should not set so quickly that it cannot be brushed out thoroughly without undue difficulty; on the other hand, it must set sufficiently rapidly to avoid the formation of streaks and tears when the varnish is applied to a vertical surface. For such tests, therefore, it is important that a fairly good size panel (at least 3 ft. by 1 ft.) should be used and that the test should be carried out in such a way as to approach actual working conditions as nearly as possible.

CHEMICAL TESTS

The application of chemical tests to varnishes and varnish materials is a matter of some difficulty, for the resins are not chemical entities and the processes which they undergo during incorporation into varnishes involve very complex, and as yet very imperfectly understood, changes both in the resins and in the other ingredients.

At the same time, even if the ultimate significance of the results of chemical tests is not clearly realised, the data correlated with those obtained by physical tests and by experience are essential to the proper control of factory operations, the matching of samples, the institution of new processes and the investigation of complaints and difficulties.

Apart from these questions, however, the systematic examination of raw materials is of great value both in preventing trouble due to faulty deliveries and providing the necessary data to justify a rejection when defective materials are offered. The fact that a firm is known to test deliveries and insists upon them being up to standard, undoubtedly enhances its reputation and consequently this custom is valued by the trade. Routine testing of supplies is therefore justified as a preventive quite apart from actual detection of faulty supplies. When faulty materials actually are delivered the accumulated record of the properties of satisfactory supplies is often essential, for in most cases the standard of comparison is relative rather than absolute. If, for example, trouble arises with cobalt driers, it is only by comparing the delivery in question with the average of previous satisfactory deliveries that one can decide whether or not the delivery is below the accepted standard and therefore the cause of the trouble.

Similarly, with oils and resins it is seldom that one has to deal with actual adulteration, but deviation from the normal is a frequent source of trouble and dispute. In all such cases the existence of complete detailed records over a long period is of vital importance and in the event of a dispute being carried to the length of arbitration or even litigation, may often prove a determining factor.

THE INTERPRETATION OF PHYSICAL AND CHEMICAL TESTS

The most important part of the physical testing of paints and varnishes is the interpretation of the results. In practice, varnishes have to withstand not only a variety of conditions, but continuous changes of conditions. Both the varnish and its support expand and contract under the influence of temperature, whilst water is either absorbed or exhaled with changes in humidity. It is important, therefore, to bear this in mind when endeavouring to assess the commercial value of a varnish on the results of laboratory tests. The standard of comparison must also be fixed in accordance with the purpose for which the varnish is to be used and any specific virtues which may be claimed for the product under consideration.

A varnish intended for interior decoration will not be judged

by the standards rightly applied to an outside varnish, whilst varnishes intended for special conditions such as, for example, those obtaining on board ships must be judged by special standards.

Any varnish applied to carriages, motor cars or rolling stock generally, must be specially elastic to withstand vibration. Such considerations have also to be taken into account in designing exposure tests.

First class varnishes are usually applied to good materials, whilst cheap varnishes are generally applied to correspondingly cheap wood, and the material used for the exposure test must be selected accordingly. An important factor in any exposure test is the treatment which the film receives in its early stages. In practice, an outside varnish has to withstand weather conditions from the moment of application. In making tests it is invariably the practice to paint the panels indoors and allow them to dry before exposing them. This may be desirable on certain classes of work in order to obtain comparative results and eliminate the element of uncertainty as to weather conditions at the moment of exposure, but it is desirable that in any test which is of importance at least one panel should be varnished *in situ*. In no case can a single panel be taken as sufficient evidence as to durability, and it is advisable to start a second series of tests some time after the first series so as to get at least some indication of the effect of weather conditions on the varnish during its early life. If one set is started during the spring a second set should be started in the summer when the general conditions are drier and the temperature changes not so violent.

Similar considerations must be borne in mind in assessing the value of all other tests. It will be found that no test is complete in itself, but taking all the selected tests together and bearing in mind the limitations of each, it will be found that work of this character soon begins to yield valuable results. With increasing experience the value of the results becomes correspondingly greater and in the course of a year or two the student will find the records invaluable.

Two important things must be said in conclusion. Results take time to mature and their value depends entirely upon the accuracy of the data and history of the test. It is therefore important to start such work at the earliest possible moment

and not wait for an emergency arising to reveal the lack of knowledge which can be obtained in no other way than by lengthy tests. It is equally important that all data should be minutely and accurately recorded in such a form that it is readily available even after a long period.

It is not proposed to give details of the various chemical tests which are described in any reliable text book but merely to comment upon the value of the various tests from the point of view of the efficient working of the varnish factory.

1. VEGETABLE OILS

Only two oils of this class appear to any extent in the varnish factory—linseed oil and China wood oil.

(a) *Linseed Oil*. The most important chemical tests are acid value and iodine value, which should certainly be carried out on every delivery. It is advisable also to determine the saponification value. Of the physical tests, colour, freedom from suspended matter and water, and the behaviour on heating to the "breaking" point are important. A drying test, both with and without driers, is also advisable.

(b) *China Wood Oil*. Here the most important tests are the polymerisation test ("Brown's Heat Test" is to be preferred, as it is invariably adopted in both British and American Specifications) and the Refractive Index. The tests are characteristic and definitive. The iodine value (which in this case must be determined with especially careful observation of standard conditions) and the acid value are important. The specific gravity is also important in view of the fact that the gravity of China wood oil is exceptionally high.

Readers are referred to the Appendix for the current method of carrying out the polymerisation test. It should be noted that the British Standard Specification for China wood oil is under review at the time of going to press, and important alterations may be made.

(c) *Other Oils*. Perilla, soya and rape oils are occasionally used and should be examined in the same way as linseed oil.

2. THINNERS

The most important thinners are turpentine and white spirit.

(a) *Turpentine*. The American variety is invariably used in this country and the properties of the standard quality have

been carefully specified. For general purposes the specific gravity, colour, distillation range and flash point are sufficient. In testing deliveries from a new or dubious source of supply it is advisable to determine the unpolymerisable matter and the refractive index.

(b) *White Spirit*. Deliveries of white spirit should be tested in accordance with the specification with which they should comply. Distillation range, flash point and freedom from discolouration are important. Attention should also be drawn to the question of sulphur content, especially in grades intended for use in white enamels. In certain types of varnish the possibility of precipitation of some of the ingredients is considerable, and therefore a practical test should be devised to determine the solvent power of the delivery with reference to the varnish in which it is to be incorporated.

(c) *Other Solvents*. Coal tar naphthas ("benzols" and "xylols") are being used to an increasing extent in varnish manufacture. The tests to be carried out are similar to those for white spirit, and in the case of "xylol" the flash point is of great importance as it invariably comes within a degree or two of the legal limit of 73° F. The use of the newer organic solvents which are generally associated with the cellulose lacquer industry is increasing in the varnish industry, but the amounts are only small. The most important is probably butyl alcohol which is used in certain types of varnishes made with resins of the Albertol type. Supplies of these should be purchased from reliable manufacturers and should conform to the specifications laid down by the British Standards Institution (B.S.I., formerly B.E.S.A.).

3. DRIERS

It is most important that driers should be of standard quality, and in view of the important part they play in determining the properties of a varnish and the fact that only relatively small quantities are used, it is false economy to buy any but the best products of reliable manufacturers. The total metal content is not always an accurate indication of drying, and therefore supplies should be tested for metal content and also for drying power according to an appropriate standard test.

4. RESINS

(a) *Oil Soluble Resins.* The value of copals is invariably assessed by mere inspection and with experience a very accurate estimate can be formed. In view of the difficulty of taking an accurate sample the value of chemical and physical tests is somewhat limited. It is desirable, however, that in addition to inspecting carefully the bulk delivery the chemist should make some tests in the laboratory, e.g., small experimental runs which often prove very useful. The melting point and general behaviour on heating under conditions similar to those obtained in actual practice are important, and a distillation test carried out under standard conditions yields useful information to the experienced operator. The moisture, ash and acidity are also of value.

(b) *Spirit Soluble Resins.* Resins of this group should be tested for solubility in the appropriate solvent. In the case of damar the solubility in white spirit of the particular grade used in the factory is of special importance as damars vary considerably in their behaviour towards this solvent and different grades of white spirit possess widely different solvent properties.

5. SHELLAC

Shellac is in a class by itself. The quality of the standard London TN grade which is most widely used is controlled by the London Shellac Users' Association, but it is desirable that the quality of supplies should be checked by the individual user. As to other grades, these are numerous and supplies should be carefully checked with special attention to the property which is most important from the point of view of the user. Colour, rosin content and solubility in alcohol or in the alkaline solutions used in making water varnishes are the most important.

6. BITUMENS, ASPHALTS AND PITCHES

These should be carefully checked by comparison with the standard sample. Behaviour on heating under standard conditions and compatibility with the other ingredients with which the sample is to be used must be tested. As these substances have no definite melting point a standard test must be adopted. The "cube in air" method is perhaps

the most suitable for use in a general laboratory. Some writers prefer the mercury method in which the temperature at which the submerged substance becomes sufficiently fluid to rise to the surface is noted. The "cube in air" method has the advantage that the specimen is under observation during the whole test and with experience the behaviour of the cube as the temperature rises is very informative. In the case of the more expensive grades (e.g., Gilsonite) it is advisable to determine accurately the insoluble matter, especially when the material is to be used in a volatile solvent.

CHAPTER XV

NOTES ON LABORATORY METHODS

THE following notes are intended to indicate the simpler methods to be used in testing varnish materials in the laboratory and to direct the reader to sources of more detailed information referred to in the Bibliography.

PHYSICAL TESTS

1. *Specific Gravity*

For approximate tests in the works a hydrometer is sufficiently accurate. It is important, however, that these hydrometers should be checked periodically in the laboratory. For more accurate work in the laboratory, the specific gravity bottle can be used. For thick liquids, the type with a wide neck can be used. All results should be calculated to 15.5° C (60° F.).

Uses.

1. Conversion of volumes to weights is necessary for costing and other operations.

2. Detection of errors in works operations such as the addition of too much or too little thinners to oil varnishes or in the quantities used in spirit varnishes.

3. As a check on the purity of raw materials or the determination of the ingredients of an unknown sample. The following cases are of particular interest :

- (a) *Linseed Oil.* Adulteration with mineral oils is indicated by a lower specific gravity. Thickened oils have a higher specific gravity and this determination is often used in grading such oils.
- (b) *China Wood Oil.* China wood oil has a higher specific gravity than any of the vegetable oils, 0.940 to 0.942 as compared with 0.930 to 0.935 for linseed oils.
- (c) *Thinners.* Petroleum hydrocarbons such as white spirit have a specific gravity in the region of 0.8

whereas turpentine and coal-tar hydrocarbons vary from about 0.86 to 0.88. This test is therefore useful in detecting the presence of white spirit in varnish thinners.

2. *Refractive Index*

This is specially important in testing China wood oil which has a higher refractive index than any other untreated vegetable oil. It is also very useful in the examination of all oils and fats. Most textbooks contain figures for the commoner substances but the authoritative compilation is that of Kanthack and Goldsmith (see Bibliography).

3. *Distillation Test*

This is extremely important in testing thinners, particularly white spirits and solvent naphthas, which should always be purchased to specification. The test must be carried out strictly in accordance with an agreed procedure. That given in the B.E.S.A. specification is to be recommended. The dimensions of the apparatus, the rate of distillation and the position of the thermometer all affect the result.

4. *Melting Point*

This test is important in testing supplies of such materials as waxes and fats which have a characteristic melting point. The fatty acids have also characteristic melting points. The capillary tube method should be used. For resins and pitches and similar materials which have very indefinite melting points, special methods are adopted which indicate the temperatures at which certain degrees of fluidity are reached. In the case of resins, the ordinary capillary tube method is of value, the temperatures at which "sintering," "softening" and complete fusion or decomposition occurs being noted. In the case of pitches, elaborate standard methods have been developed to suit special cases (see Langton, Bibliography).

CHEMICAL TESTS

1. *Acid Value*

This is defined as the number of milligrammes of potassium hydroxide required to neutralise the free acids in one gram of a substance. In the case of oils and alcohol-soluble resins

such as rosin and shellac, alcohol may be used as a solvent. For other resins a mixture of equal parts alcohol and benzene is to be preferred. Phenolphthalein is used as an indicator in all cases. The determination is of importance :—

1. In testing raw and refined oils. A high acid value denotes either improper refining or an impure product.

2. As a check on the quality and purity of natural resins. Rosin the cheapest resin has a high acid value.

3. In the determination of the extent to which a resin has been esterified.

4. As a check on the quality of a varnish and consistency in the manufacturing process.

5. Paint and enamel media to be used in conjunction with basic pigments must be of low acidity and the acid value must therefore be carefully observed.

2. *Ester Value and Saponification Value*

The ester value is defined as the number of milligrammes of potash required to saponify the esters present in 1 gm. of a substance. The sum of the acid value and the ester value is the saponification value, i.e., the number of milligrams of potash required to saponify one gram of the substance. The determination is of importance as a check on the purity of vegetable oils which consist almost wholly of saponifiable matter. It is of little value in the examination of resins.

3. *Iodine Value*

This is defined as the percentage of iodine which combines with a substance under certain conditions. It is essential that the test should be carried out with rigid adherence to the conditions laid down in the standard test. In practice, the Wijs method of carrying out the test is invariably used. Unless the conditions of the test are carefully observed reactions other than the addition of iodine to the unsaturated substance may occur. This is particularly the case with shellac, rosin and China wood oil. The test is of importance in determining the degree of unsaturation of an oil and hence its drying property. It is of little use in the case of resins apart from shellac, in which case it is the recognised means by which the rosin content is determined.

4. *Colour Reactions*

Numerous colour reactions have been described for the purpose of identifying qualitatively various oils and resins. In the case of oils these are not of any great importance, but in the case of resins they have been proved of value in the hands of experienced workers. Reference must be made to the literature for details of most of these but it should be pointed out that it is only by actual experience with samples of known constitution and origin that one can make use of such tests with any confidence. The most generally used tests are the Storch-Morawski test for rosin and the Halphen-Hicks test which gives characteristic colours with rosin and other resins.

1. *The Storch-Morawski Test.* The test is based on the fact that the addition of a drop of strong sulphuric acid (specific gravity 1.8) to a solution of rosin in acetic anhydride produces a violet colour which rapidly fades to a purple and finally becomes a dirty red-brown. Various other substances give a reddish colour in this test, and if the amount of rosin is small the results are indefinite. In the case of complex mixtures, a preliminary separation of the rosin must be made. The simplest method is to extract the substance with hot alcohol and filter on cooling. The rosin remains in solution, and on evaporation of the alcohol the test can be applied. For important work the modification suggested by Wolff is the most satisfactory (see T. H. Barry, p. 208).

2. *The Halphen-Hicks Test.* This test is particularly useful in testing the resins extracted from a varnish by the methods to be mentioned later. It depends upon the fact that if a solution of the resin in carbon tetrachloride with a little phenol added is brought into contact with bromine vapour a more or less characteristic series of colours is developed. Thus rosin gives a green colour which rapidly changes to blue and violet whilst kauri gives a blue colour which changes to purple. In the case of shellac the test is very useful in detecting the presence of rosin (see Barry p. 262). It is important, however, that any conclusions drawn from these colour changes should be confirmed by comparison with standard samples which have undergone similar treatment (see Fox and Bowles, p. 160 and Barry, p. 36).

NOTES ON THE ANALYSIS OF OIL VARNISHES

For the detailed examination of the oils and resins present in oil varnishes no complete scheme can be formulated. The following indicate the main lines of procedure and references are given to the most readily accessible books in which the subject is discussed in detail.

It should be emphasised, however, that considerable manipulative skill and practical experience is essential, and further, that the references given are only to be regarded as preliminary. The original references which are given in the text books referred to should be followed up and the analyst must always be prepared to modify or add to the recommended procedure in order to cope with specific cases.

PROCEDURE I

Treatment with ice-cold petroleum ether (see Fox and Bowles, p. 168). This effects a more or less complete separation into (a) oil and rosin which are soluble (b) resins and oxidised oils which are insoluble. Further separation can be effected as follows :

1. Saponification and separation of the acids. Acids from oxidised oils are insoluble in petroleum ether and soluble in ether. Esterification of the petroleum ether-soluble acids. Resin acids are not esterified, fatty acids are esterified. The esters of the fatty acids can be saponified and the acids liberated.

*2. China wood oil, if present, can be estimated on a portion of the original petroleum ether solution by Goldsmith's method (see Fox and Bowles, p. 168).

PROCEDURE II

In this scheme the varnish from which the bulk of the thinners has been removed by boiling with small successive quantities of water is treated under reflux with alcoholic potash and the mixture of fatty and resin acids and unsaponifiable matter used in further tests—in this way the metals are removed and the procedure simplified.

The mixture thus obtained consists of :

1. Soaps of oils and resins.
2. Unsaponifiable matter of resins.
3. Oxides and hydroxides of metals.

On evaporating the alcohol and treating with hot water followed by excess of hydrochloric acid there is obtained :

1. Salts of metals, soluble in water.
2. Acids of resins and oils soluble in petroleum ether.
3. Unsaponifiable matter soluble in petroleum ether.

4. Unsaponifiable matter from resins insoluble in petroleum ether.

5. Oxyacids insoluble in petroleum ether.

The aqueous solution of metallic salts is separated in the usual way by either Twitchell's or Scholze's method.

The mixture of fatty and resin acids is esterified. The resin acids are not affected and can be removed by treatment with cold alcoholic potash. The esters of the fatty acids can be saponified and the acids recovered for further examination. China wood oil is tested for on the petroleum ether solution as described above.

The unsaponifiable matter insoluble in petroleum ether is a resinous mass which adheres to the flask and can be easily separated from the other portions. It should be very thoroughly washed with hot water and then with petroleum ether and the washings added to the main portion in the separating funnel.

The oxyacids of linseed oil are readily soluble in ether and distinguished from the oxyacids of rosin by their insolubility in N/2 alcoholic NaOH and in 70 per cent acetone.

In addition to these and special tests the price of the varnish, the purpose for which it is to be used, the nature of the film and the odour on burning a dried film are all of great assistance to the analyst as suggesting the most likely ingredients and the materials from which a match for the sample can be made. In view of the fact that the properties of a varnish are so largely determined by the methods of manufacture the main purpose of the analyst is invariably to discover by what processes the available materials can be made up into a substantially identical product.

BITUMINOUS COMPOSITIONS

The methods are similar to those described under oil varnishes. The bitumens used in the varnish industry are practically insoluble in petroleum ether and the saponifiable matter rarely exceeds 15 per cent. Gilsonite, the most commonly occurring natural bitumen, contains practically none. Stearin and allied pitches usually contain over 50 per cent saponifiable matter and have a fairly high acid value. They are only partially soluble in petroleum ether but the solubility is affected by the presence of vegetable oils. They impart a fairly characteristic rubbery consistency to the petroleum ether insoluble fraction. C. D. Holley's book should be consulted for a detailed discussion of the subject.

APPENDIX

HEATING TEST (BROWNE'S METHOD) FOR CHINA WOOD OIL

TEST tubes for containing the oil should be 16 cm. by 15 mm. with a mark near the bottom to indicate 5 cc., and closed by a cork so perforated that a glass rod 3 mm. diameter can move freely.

Fill a copper beaker (height, 12 cm. ; internal diameter, 6 cm.) with cotton-seed oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath.

Use a nitrogen-filled immersed-stem chemical thermometer, engraved stem ; total length 4 to 4½ in. ; graduated from 210° to 310° C. in 2° intervals ; the length between 210° and 310° C. not less than 2½ in. If preferred, use emergent-stem thermometer 30 cm. long, with graduations from 100° to 400° C., making correction for emergent stem according to the method outlined in Stem Correction Sheet No. 44 of the U.S. Bureau of Standards.

Procedure. When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 cc. of the oil to be tested so that its bottom is level with the lowest part of the bulb of the thermometer. Note the time ; remove the source of heat for about forty-five seconds, and then re-apply. Before two minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the tung oil has been in the bath about nine minutes, raise the glass rod at intervals of 15 seconds, and when the rod is firmly set note the time. As setting or jellying takes place within a few seconds after the state of fluidity first changes to a "stringy" condition, a good end determination is afforded. Remove the specimen at once, heat the bath again to 293° C., and repeat the experiment with another portion of the sample. No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached and controlled. When the cotton-seed oil has become tarry and viscid, it should be renewed ; otherwise heating may be irregular.

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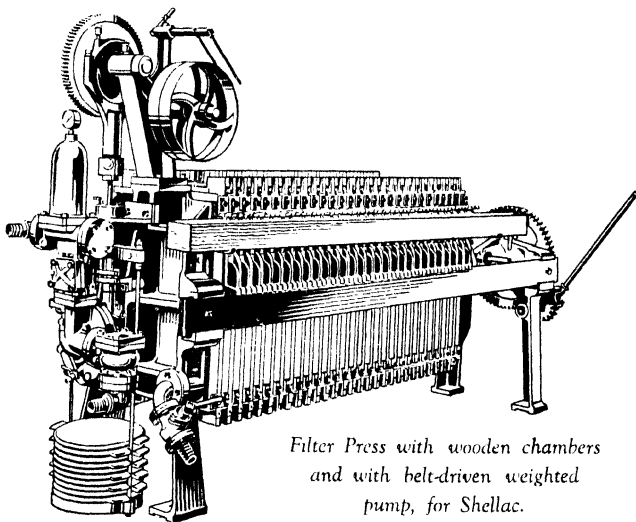
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